



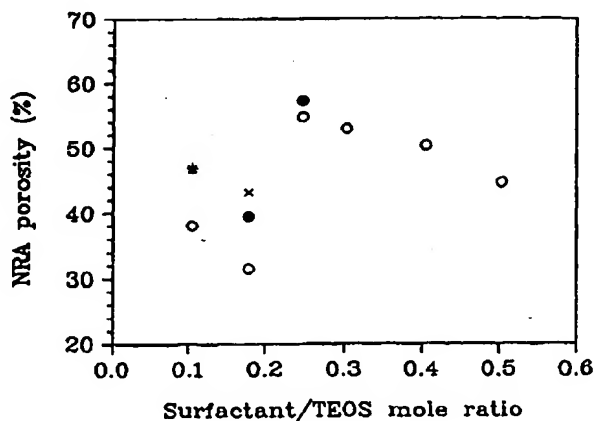
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(54) Title: MESOPOROUS SILICA FILM FROM A SOLUTION CONTAINING A SURFACTANT AND METHODS OF MAKING SAME

(57) Abstract

The present invention is a mesoporous silica film having a low dielectric constant and method of making having the steps of combining a surfactant in a silica precursor solution, spin-coating a film from this solution mixture, forming a partially hydroxylated mesoporous film, and dehydroxylating the hydroxylated film to obtain the mesoporous film. It is advantageous that the small polyoxyethylene ether surfactants used in spin-coated films as described in the present invention will result in fine pores smaller on average than about 20 nm. The resulting mesoporous film has a dielectric constant less than 3, which is stable in moist air with a specific humidity. The present invention provides a method for superior control of film thickness and thickness uniformity over a coated wafer, and films with low dielectric constant. The present invention is a method of dehydroxylating a silica surface that is hydroxylated having the steps of exposing the silica surface separately to a silicon organic compound and a dehydroxylating gas. Exposure to the silicon organic compound can be in liquid, gas or solution phase, and exposure to a dehydroxylating gas is typically at elevated temperatures. In one embodiment, the improvement of the dehydroxylation procedure is the repetition of the soaking and dehydroxylating gas exposure. In another embodiment, the improvement is the use of an inert gas that is substantially free of hydrogen. In yet another embodiment, the present invention is the combination of the two-step dehydroxylation method with a surfactant templating method of making a mesoporous film.

NRA porosity - C_xEO₁₀ series

- + C₁₈EO₁₀ (XL-91 sample series)
- C₁₆EO₁₀ (XL-132 sample series)
- C₁₆EO₁₀ (XL-90 series)
- × C₁₂EO₁₀ (XL-92 series)

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MESOPOROUS SILICA FILM FROM A SOLUTION CONTAINING A SURFACTANT AND METHODS OF MAKING SAME

This invention was made with Government support under Contract
5 DE-AC0676RLO1830 awarded by the U.S. Department of Energy. The Government has
certain rights in the invention.

CROSS REFERENCE TO RELATED INVENTION

This application claims priority from application serial numbers 09/220,882, filed
10 December 23, 1998, 09/335,210, filed June 17, 1999, 09/361,499, filed July 23, 1999,
09/222,569, filed December 28, 1998, and 09/413,062, filed October 4, 1999. This
application is a Continuation-In-Part of application serial number 09/413,062, filed October
4, 1999, now pending, which is a Continuation-In-Part of application serial number
09/361,499, filed July 23, 1999 now pending, which is a Continuation-in-Part of application
15 serial number 09/335,210, filed June 17, 1999, now pending, which is a Continuation-In-Part
of application serial number 09/222,569, filed December 28, 1998, now pending, which is a
Continuation-In-Part of application serial number 09/220,882 filed December 23, 1998, now
abandoned.

20 FIELD OF THE INVENTION

The present invention relates generally to porous silica film with nanometer-scale
porosity produced from solution precursors. More specifically, the present invention relates
to mesoporous silica film from a solution-containing a surfactant (surfactant templated) and
the use of specific surfactants to template porosity with the characteristic pore size being
25 defined by the surfactant micelle size. The present invention also relates to the use of
dehydroxylation in combination with surfactant templated mesoporous silica films to obtain a
dielectric constant less than 3 under ambient humid conditions.

As used herein, the term "silica" means a compound having silicon (Si) and oxygen (O)
and possibly additional elements.

30 Further, as used herein, "mesoporous" refers to a size range which is greater than 1 nm,
but significantly less than a micrometer. In general, this refers most often to a size range
from just over 1.0 nm (10 angstroms) to a few tens of nanometers.

The term "stable" can mean an absolute stability, a relative stability or a combination thereof. Relative stability means that a dielectric constant increases no more than about 20% when a surfactant templated mesoporous film is taken from an equilibrated condition of 0.0% relative humidity or vacuum to an equilibrated condition of 50% relative humidity. Absolute stability means that the dielectric constant remains less than 3 under any conditions including humid conditions of at least 40% relative humidity.

The term "hydroxylated" encompasses partially and fully hydroxylated. The term "dehydroxylating" encompasses partial or total removal of hydroxyl groups from surface(s) of the surfactant templated mesoporous silica film.

BACKGROUND OF THE INVENTION

Porous silica films are potentially useful as low dielectric constant intermetal materials in semiconductor devices, as low dielectric constant coatings on fibers and other structures, and in catalytic supports. Most of the U.S. semiconductor industry is presently (1998) in the process of implementing interlevel dielectric films that are silica films, or derivatives of silica and silicates, or polymeric films, with less than 25% or no porosity with dielectric constant (k') in the range of 3.0 to 4.0. Further reductions in dielectric constant are desired to improve the operating speed of semiconductor devices, reduce power consumption in semiconductor devices and reduce overall cost of semiconductor devices by decreasing the number of metallization levels that are required.

Since air has a dielectric constant of 1.0, the introduction of porosity is an effective way of lowering the dielectric constant of a film. In addition, because silica dielectrics have been a standard in microelectronic devices, silica films with porosity are very attractive to the semiconductor industry for advanced devices that require low dielectric constant materials. The feature size or design rule in the semiconductor interconnect will be sub-150 nm in ultralarge scale integration; and pore sizes to achieve lower dielectric constant ($k < 3$) must be significantly smaller than the intermetal spacing.

Dielectric constant of porous films is dependent on the material and pore structure. For porous silica films for use in microelectronic devices, material and pore structure must result in uniform dielectric constants across the wafers and in different directions on the wafer. In general, isotropic material and pore structures are expected to provide the desired uniformity in film dielectric constant compared to anisotropic material and pore structures.

Also, low dielectric constant mesoporous films used commercially need to be prepared in a manner compatible with a semiconductor device manufacturing process line, for example spin coating. For large-area circular wafers, other coating techniques such as dip coating are not as convenient because dip coating requires masking of the backside to prevent
5 contamination.

Surface topography is also very critical to fabrication of a multilevel interconnect structure. In the "damascene" process for copper interconnects intended for ultralarge scale integration on semiconductor chips, each dielectric layer is etched, following which copper is deposited, and the structure planarized by chemical-mechanical polishing (CMP). The initial
10 planarity and the absence of surface texture in the low k dielectric film is very critical in maintaining planarity at each level of the interconnect.

Another important concern with porous dielectric films is mechanical integrity. Because of their fragility, it appears unlikely that porous films will be directly polished using conventional chemical-mechanical-polishing (CMP) equipment, but a dense "cap" layer of
15 silica or another material on the porous low K film will be planarized. However, even with a cap layer, the porous low K material must have adequate stiffness, compressive and shear strengths, to withstand the stresses associated with the CMP process.

Silica films with nanometer-scale (or mesoporous) porosity may be produced from solution precursors and classified into two types (1) "aerogel or xerogel" films
20 (aerogel/xerogel) in which a random or disordered porosity is introduced by controlled removal of an alcohol-type solvent, and (2) "mesoporous" surfactant-templated silica films in which the pores are formed with ordered porosity by removal of a surfactant. Heretofore, the most successful demonstration of low dielectric constant silica films with dielectric constant of 3.0 or less has been with aerogel/xerogel-type porous silica films. However, disadvantages
25 of aerogel/xerogel films include (1) deposition of aerogel/xerogel films requires careful control of alcohol removal (e.g. maintaining a controlled atmosphere containing solvent or gelling agent during preparation) for formation of the pore structure (2) the smallest pore size typically possible in aerogel/xerogel films falls in the size range of 10-100 nm, and (3) limited mechanical strength compared to dense silica films. These disadvantages have
30 hindered implementation of these aerogel/xerogel porous silica films in semiconductor devices.

In order to obtain a porous film with a low dielectric constant of any material made by any process, it is necessary to minimize the number of hydroxyl groups in the structure, especially at pore surfaces. The dielectric films must be made hydrophobic in order for the electrical properties to be stable in humid air. Hydroxylated surfaces in porous silica films result in a dielectric constant exceeding that of dense silica (i.e. approximately 4.0).

Physisorption of water molecules by hydroxylated surfaces can further increase the dielectric constant and effective capacitance of a mesoporous silica film. Physisorption of water molecules can be avoided by handling films in non-humid atmospheres or vacuum, or by minimizing exposure of films to humid conditions. Hydroxyl groups and physisorbed water molecules may be removed from silica surfaces at very high temperatures. C. J. Brinker and G. W. Scherer, in Sol-Gel Science, Academic Press, New York, NY (1990) (Brinker et al. 1990) discuss thermal dehydroxylation of silica by exposure to very high temperatures of over 800°C. However, semiconductor devices with dielectric films and metal lines cannot usually be processed over about 500°C. Thus, other methods of dehydroxylation are needed for porous silica films on semiconductors.

E. F. Vansant, P. Van der Voort and K. C. Vrancken, in Characterization and Chemical Modification of the Silica Surface, Vol. 93 of Studies in Surface Science and Catalysis, Elsevier, New York, NY (1995), and Brinker et al., 1990, cite procedures for hydroxylation of silica surfaces by fluorination or by treatment with silane solutions.

Aerogel/Xerogel-type films have been dehydroxylated by both (a) fluorination treatment, and (b) a two-step dehydroxylation method of (1) initial silane solution treatment (e.g. trimethylchlorosilane or hexamethyldisilazane (HMDS) in a solvent), and then (2) following this solution treatment with a treatment in hydrogen-containing gases (e.g. 10% hydrogen in nitrogen) at moderately high temperatures of 300-450°C. The silane/forming gas(H_2 in N_2) treatment is discussed in US patent #5,504,042 and some of the other related patents by Smith and colleagues that are referenced therein.

In the surfactant-templated films, the pores form ordered (e.g. hexagonal) arrays, with the characteristic pore size being defined by the surfactant micelle size. The surfactant templated route allows control of the porosity, pore size and pore shape using the properties of the surfactants and their interactions with the silica species. For a given level of porosity, this control in pore size and architecture and structure of the pore walls can also result in good mechanical properties. More specifically, smaller and uniform pores can impart better

mechanical properties than larger and non-uniform pores. Although easier to produce (no need for controlled atmosphere to form the porosity), mesoporous surfactant templated silica films have not been demonstrated with low dielectric constant.

US Patent application 08/921,754 filed 08/26/97 by Bruinsma et al, now U.S. patent 5,922,299, describes the preparation of mesoporous surfactant templated silica films with ordered porosity by spin coating. The surfactant used was a cationic ammonium-based surfactant. A goal of this work was low-dielectric constant interlayers in microelectronic devices.

US patent 5,858,457 by Brinker et al also reports a dip coating procedure for making a surfactant-templated mesoporous silica film with ordered porosity, where the surfactant used was also a ammonium-based surfactant. Brinker et al measured the dielectric constant using a mercury dot electrode on the film, reporting a value for the dielectric constant of 2.37.

However, surfactant templated mesoporous silica films prepared with ammonium surfactants and tested after pyrolysis (thermal removal) of the surfactant have been found to adsorb moisture under ambient humid conditions, and therefore do not have a low dielectric constant under the ambient humid conditions of normal manufacturing and operating conditions for semiconductor devices. No dehydroxylation steps are reported in either Bruinsma et al. or Brinker et. al.

The paper Continuous Mesoporous Silica Films With Highly Ordered Large Pore Structures, D. Zhao, P. Yang, N. Melosh, J. Feng, BF Chmelka, and GD Stucky, Advanced Materials, vol. 10 No. 16, 1998, pp 1380-1385, discusses the formation of directional or ordered large pore structures in films by dip coating silica based solutions containing non-ionic poly(alkylene oxide) triblock copolymers and low molecular weight alkyl(ethylene oxide) surfactants. Low dielectric constants (1.45 – 2.1) were reported for these films as measured after calcination of the films. However, a disadvantage of ordered porosity, for example hexagonal porosity, is the uncertainty in uniformity of dielectric constant in different directions on large wafers. Furthermore, no dehydroxylation procedures, that are useful for maintaining low values of dielectric constant, are reported in the paper by Zhao et al.

Thus, there is a need for a surfactant templated mesoporous silica films and method of making them that provides a dielectric constant less than 3, and that meets engineering requirements including but not limited to control of film thickness and thickness uniformity, minimum surface texture, and mechanical integrity. The dielectric constant must be

relatively stable under normal operating conditions which include humid air at room temperature, and must be uniform across large wafers.

SUMMARY OF THE INVENTION

5 It is therefore an object of the present invention to provide a surfactant templated mesoporous silica film which has properties including but not limited to dielectric constant less than 3, film thickness from about 0.1 μm to about 1.5 μm , standard deviation of film thickness less than or equal to $\pm 5\%$ standard deviation, average pore sizes smaller than about 20 nm, low dielectric constant and combinations thereof.

10 The present invention includes a method of making a surfactant templated mesoporous film having the same general steps as described in co-pending application serial no. 08/921,754, now U.S. patent no. patent 5,922,299 entitled MESOPOROUS-SILICA FILMS, FIBERS AND POWDERS BY EVAPORATION. Thus, the present invention is a method of making a mesoporous silica film having the steps of combining a surfactant in a
15 silica precursor solution, spin-coating a film, heating the film to remove the surfactant to form a mesoporous film that is at least partially hydroxylated, and dehydroxylating the partially hydroxylated film to obtain the mesoporous film. According to the present invention, selection of surfactant, selection of concentrations of silica precursor solution constituents and combinations thereof provide a film having one or more of the features set
20 forth above.

The advantage of low dielectric constant ($k < 3$) that is stable at ambient humid conditions is achieved in accordance with the present invention in combination with dehydroxylation which involves partial or complete removal of hydroxyl groups at temperatures within electronic component processing temperatures. During dehydroxylation,
25 hydroxyl groups may be replaced with hydrophobic groups such as organic alkyl groups, siloxane (-Si-O-Si-) bonds or combinations thereof on internal pore surfaces as well as external surfaces of the surfactant templated mesoporous film.

It is advantageous that the surfactants used in spin-coated surfactant templated mesoporous films as described in the present invention will result in fine pores smaller than
30 about 20 nm. Most often the average pore size can be tailored with surfactants in the size range of about 1 to about 20 nm. This pore size range is desirable in interlevel dielectric films that separate metallization lines in semiconductor devices to minimize diffusion of metal species during repeated heat treatments. Further advantages of the present invention

include a method which provides for superior control of film thickness and thickness uniformity across a coated wafer, films with low dielectric constant that is stable; as well as disordered porosity which increases confidence in uniformity of dielectric constant in different directions on large wafers.

5 It is a further object of the present invention to provide a method of dehydroxylating a silica surface that is hydroxylated in order to obtain a low dielectric constant.

It is further an object of the present invention to provide methods of making mesoporous silica film, which result in low dielectric constant and permit spin-coating techniques that do not require atmospheric controls. These methods of making mesoporous silica film further provide for superior control of film thickness and average pore diameter
10 smaller than 5 nm. The present invention differs from the aerogel method through the use of specific surfactant molecules to template porosity in spin-coated films.

Thus, the present invention further involves method of dehydroxylating a silica surface that is hydroxylated having the steps of exposing the silica surface separately to a silicon organic compound and a dehydroxylating gas. The silicon organic compound is also
15 known as a silylation agent. Exposure to the silicon organic compound can be in liquid, gas or solution phase, and exposure to a dehydroxylating gas is typically at elevated temperatures. The present invention has the advantages of providing a mesoporous film of a silica material having low dielectric constant that is stable over time. Further advantages of the present invention potentially include improved safety and lower cost when applied on a
20 large scale.

In one embodiment, the improvement of the dehydroxylation procedure is the repetition of the soaking and dehydroxylating gas exposure. In another embodiment, the improvement is the use of an inert gas that is substantially free of hydrogen.

25 In yet another embodiment, the present invention is the combination of the two-step dehydroxylation method with a surfactant templating method of making a mesoporous film. The method of making a mesoporous silica film has the general steps as described in co-pending patent application 08/921,754 hereby incorporated by reference, viz: combining a surfactant in a silica precursor solution, spin-coating a film, and heating the film to remove
30 the surfactant to form a mesoporous film that is at least partially hydroxylated, and dehydroxylating the hydroxylated film to obtain the mesoporous film. According to the present invention, the improvement comprises dehydroxylation of the hydroxylated film with

the two-step dehydroxylation of exposing the hydroxylated film separately to a silicon organic compound and to a dehydroxylating gas to obtain a mesoporous film with low dielectric constant.

Further improvements are realized for any of the above referenced embodiments by using a polyoxyethylene ether compound as the surfactant.

It is advantageous that the small polyoxyethylene ether surfactants used in spin-coated films as described in the present invention will result in fine pores smaller than about 5 nm. Most often the average pore diameter can be tailored with surfactants in the size range from about 2 to about 5 nm. This average pore diameter range is desirable in interlevel dielectric films that separate metallization lines in semiconductor devices to minimize diffusion of metal species during repeated heat treatments. These small polyoxyethylene ether surfactants are different from large polyalkylene oxide "block co-polymer" surfactants used to make fibers with pores larger than 5 nm. Further advantages of the present invention include a method which provides for superior control of film thickness and thickness uniformity across a coated wafer, films with low dielectric constant, and spin-coating techniques which do not require atmosphere controls.

The subject matter of the present invention is particularly pointed out and distinctly claimed in the concluding portion of this specification. However, both the organization and method of operation, together with further advantages and objects thereof, may best be understood by reference to the following description taken in connection with accompanying drawings wherein like reference characters refer to like elements.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows film porosity as a function of surfactant/TEOS mole ratio in a spin-coating solution containing polyoxyethylene ether surfactants as determined by nuclear reaction analysis (NRA) for the C_xEO_{10} polyoxyethylene ether surfactant series.

FIG. 2 shows the dielectric constant (measured at room temperature under ambient conditions in humid air) of a surfactant templated mesoporous film prepared with $C_{12}EO_{10}$ polyoxyethylene ether surfactant as a function of dehydroxylation procedures.

FIG. 3 shows the dielectric constant (measured at room temperature under ambient conditions in humid air) of a surfactant templated mesoporous film prepared with $C_{16}EO_{10}$ polyoxyethylene ether surfactant as a function of dehydroxylation procedures.

FIG. 4a shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{12}EO_{10}$ polyoxyethylene ether surfactant. The x-ray beam was along the radial direction of the circular wafer.

FIG. 4b shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{12}EO_{10}$ polyoxyethylene ether surfactant. The x-ray beam was along the tangential direction of the circular wafer.

FIG. 5 is a transmission electron micrograph showing microstructure of the mesoporous silica film prepared with a $C_{12}EO_{10}$ polyoxyethylene ether surfactant.

FIG. 6a is a surface contour map of a mesoporous silica film prepared with a $C_{12}EO_{10}$ polyoxyethylene ether surfactant.

FIG. 6b is a surface profile of a mesoporous silica film prepared with a $C_{12}EO_{10}$ polyoxyethylene ether surfactant.

FIG. 7 is a graph of elastic modulus of a mesoporous silica film measured by picoindentation, as a function of the indentation load.

FIG. 8a shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{12}EO_{10}$ polyoxyethylene ether surfactant. Surfactant/TEOS mole ratio was 0.19. The x-ray beam was along the radial direction of the circular wafer.

FIG. 8b shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{12}EO_{10}$ polyoxyethylene ether surfactant. Surfactant/TEOS mole ratio was 0.19. The x-ray beam was along the tangential direction of the circular wafer.

FIG. 9a shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{12}EO_{10}$ polyoxyethylene ether surfactant. Surfactant/TEOS mole ratio was 0.30. The x-ray beam was along the radial direction of the circular wafer.

FIG. 9b shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{12}EO_{10}$ polyoxyethylene ether surfactant. Surfactant/TEOS mole ratio was 0.30. The x-ray beam was along the tangential direction of the circular wafer.

FIG. 10a shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a mixture of $C_{12}EO_{10}$ and $C_{12}EO_4$ polyoxyethylene ether surfactant. The total surfactant to TEOS mole ratio was 0.20. The x-ray beam was along the radial direction of the circular wafer.

FIG. 10b shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a mixture of $C_{12}EO_{10}$ and $C_{12}EO_4$ polyoxyethylene ether surfactant. The total

surfactant to TEOS mole ratio was 0.20. The x-ray beam was along the tangential direction of the circular wafer.

FIG. 11a shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{16}EO_{10}$ polyoxyethylene ether surfactant. Surfactant/TEOS mole ratio was 0.20. The x-ray beam was along the radial direction of the circular wafer.

FIG. 11b shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{16}EO_{10}$ polyoxyethylene ether surfactant. Surfactant/TEOS mole ratio was 0.20. The x-ray beam was along the tangential direction of the circular wafer.

FIG. 12a shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{18}EO_{10}$ polyoxyethylene ether surfactant. Surfactant/TEOS mole ratio was 0.20. The x-ray beam was along the radial direction of the circular wafer.

FIG. 12b shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{18}EO_{10}$ polyoxyethylene ether surfactant. Surfactant/TEOS mole ratio was 0.20. The x-ray beam was along the tangential direction of the circular wafer.

FIG. 12c shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{18}EO_{10}$ polyoxyethylene ether surfactant. Surfactant/TEOS mole ratio was 0.20. The x-ray beam was along the radial direction of the circular wafer. The area scanned was located about 90 degrees (rotation) away from the area scanned in Figure 12a and b.

FIG. 12d shows the low angle x-ray diffraction spectrum for mesoporous silica film prepared with a $C_{18}EO_{10}$ polyoxyethylene ether surfactant. Surfactant/TEOS mole ratio was 0.20. The x-ray beam was along the tangential direction of the circular wafer. The area scanned was located about 90 degrees (rotation) away from the area scanned in Figure 12a and b.

FIG. 13 is a graph of dielectric constant versus time for various mesoporous materials.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention is a mesoporous silica film made from a surfactant containing solution (surfactant templated mesoporous silica film) which has properties including but not limited to a dielectric constant less than 3, film thickness from about 0.1 μm to about 1.5 μm , also from about 0.2 μm to about 1.5 μm , standard deviation of film thickness less than or equal to $\pm 5\%$ standard deviation, average pore sizes smaller than about 20 nm, more preferably less than about 10 nm and most preferably less than about 5 nm, ordered or

disordered porosity, and combinations thereof. According to the present invention, porosity is greater than 30%, preferably greater than 40% and more preferably greater than 50%.

The present invention includes a method of making a mesoporous silica film by templating and spin-coating silica precursor solutions containing a surfactant to form a hydroxylated film which are the same general steps as described in co-pending patent application 08/921,754, and that application is thus incorporated herein by reference, and then chemically dehydroxylating the hydroxylated film to form the mesoporous silica film. Therefore, the present invention is a method of making a mesoporous silica film having the steps of combining a surfactant in a silica precursor solution, forming a film by spin-coating, heat treating the film to remove the surfactant and forming a mesoporous film that is hydroxylated, and chemically dehydroxylating the hydroxylated film to obtain the mesoporous silica film with a low dielectric constant.

The silica precursor solution includes a silica precursor, an aqueous solvent, a catalyst and a surfactant. A film is made by spin-coating a mixture of the silica precursor solution and surfactant, after which the aqueous solvent, the catalyst, and the surfactant are removed by heating to form mesoporous silica film that is hydroxylated. Chemically dehydroxylating the hydroxylated film results in a mesoporous silica film with a low dielectric constant. The chemical dehydroxylating is preferably achieved by exposing the hydroxylated film separately to a silicon-based organic compound such as a silane, either as the pure liquid or pure vapor or as a solution, or as a vapor in a carrier gas or gas mixture, and a dehydroxylating gas. The resulting mesoporous film has a dielectric constant less than 3 that remains less than 3 in a humid environment.

According to a further preferred embodiment of the present invention, low dielectric constant ($k < 3$) mesoporous surfactant-templated films may be obtained by using one or more dehydroxylation step(s) that includes removing hydroxyl groups from surfaces of the mesoporous material. In this embodiment, the surfactant may be any surfactant including but not limited to non-ionic surfactant, cationic surfactant, anionic surfactant, amphoteric surfactant, and combinations thereof.

The precursor solution may include a chemical agent including but not limited to a second surfactant, a smaller hydrophilic molecular compound, an organic co-solvent and combinations thereof. A second surfactant includes but is not limited to non-ionic surfactant, cationic surfactant, anionic surfactant, amphoteric surfactant and combinations thereof.

Smaller hydrophilic molecular compound includes but is not limited to glycerol, propylene glycol, ethylene glycol and combinations thereof. Organic co-solvent includes but is not limited to mesitylene, octane and combinations thereof.

The silica precursor includes but is not limited to tetraethyl orthosilicate (TEOS),
5 tetramethyl orthosilicate (TMOS) methyl triethoxysilane, phenyl triethoxy silane, dimethyl dimethoxy silane, ethyl triethoxysilane and combinations thereof.

In a preferred embodiment, the aqueous solvent includes ethanol.

The catalyst includes but is not limited to inorganic acid including but not limited to hydrochloric acid, nitric acid, sulfuric acid; organic acid including but not limited to
10 carboxylic acid, amino acid and combinations thereof. Carboxylic acid includes but is not limited to methanoic acid (formic acid), ethanoic acid (acetic acid), ethandioic acid (oxalic acid), butanoic acid (butyric acid), and combinations thereof. Amino acid includes but is not limited to glycine, nitromethane and combinations thereof.

A preferred non-ionic surfactant is a polyoxyethylene ether surfactant. The term
15 "non-ionic" refers to a surfactant chemistry where cationic (e.g. ammonium or sodium ions) or anionic (e.g. sulfonate, sulfate or halide) species are not present. The non-ionic polyoxyethylene ether surfactants described in this application are small molecules containing carbon, hydrogen and oxygen, with only a hydroxyl (-OH) group at the hydrophilic end of the polymer. With the use of these surfactants, in combination with the
20 dehydroxylation procedure, low dielectric constants (i.e. low capacitance in films) are obtained using simple synthesis and processing conditions. Additionally, greater film thickness uniformity, minimum surface texture, and stability of dielectric constant are obtained through the use of these surfactants.

Surfactants in this polyoxyethylene ether family include but are not limited to $C_{12}H_{25}$
25 $(CH_2CH_2O)_{10}OH$ also known as $C_{12}EO_{10}$ or 10 lauryl ether; $C_{16}H_{33}(CH_2CH_2O)_{10}OH$ also known as $C_{16}EO_{10}$ or 10 cetyl ether; $C_{18}H_{37}(CH_2CH_2O)_{10}OH$ also known as $C_{18}EO_{10}$ or 10 stearyl ether; $C_{12}H_{25}(CH_2CH_2O)_4OH$ also known as $C_{12}EO_4$ or 4 lauryl ether; $C_{16}H_{33}(CH_2CH_2O)_2OH$ also known as $C_{16}EO_2$ or 2 cetyl ether, and combinations thereof.

Additionally, polyoxyethylene ether surfactant may be used in conjunction with a
30 chemical agent including but not limited to other surfactants, smaller hydrophilic molecular compounds compatible with the ethanol and water present in the aqueous solvent, organic co-solvents compatible with the surfactant(s) and combinations thereof. The surfactants include

but are not limited to ammonium-based cationic surfactants such as cetyl trimethyl ammonium chloride. The organic co-solvents include but are not limited to mesitylene, octane and combinations thereof. The smaller hydrophilic molecular compounds include but are not limited to glycerol, propylene glycol, ethylene glycol, and combinations thereof. The smaller hydrophilic molecular compounds have much higher boiling points compared to water and ethanol as well as low vapor pressures. These smaller hydrophilic molecular compounds are likely to reside as inclusions in the silica-rich walls that have formed around the surfactant micelles upon spin-coating and drying, and upon calcination, these inclusions can leave behind finer scale porosity in the silica walls.

The silica precursor solution is made up of four solution compounds of (1) a silica precursor, preferably tetraethyl orthosilicate (TEOS); (2) an aqueous solvent, for example, ethanol, water and combinations thereof; (3) a catalyst for hydrolysis of the silica precursor, preferably an acid, for example nitric acid or hydrochloric acid, and (4) a surfactant. Because TEOS is not soluble in water alone, a co-solvent, preferably ethanol, is added. Although a preferable solution mixture contains mole ratios of: TEOS 1.0; water 5; ethanol 5; HCl 0.05; and surfactant 0.17, the surfactant/TEOS mole ratio can be varied to control the pore-volume fraction in the final film and to vary the pore structure. Also, it will be recognized by those skilled in the art that a much wider range of surfactant sizes and amounts in this family of small polyoxyethylene ethers may be possible with different solvent amounts. It is important to avoid precipitation of the silica precursor in the solution prior to spin coating. Precipitation of the silica precursor may be avoided by the use of alcohol as a co-solvent, preferably as a primary solvent, in combination with acidic pH. Alternatively, precipitation may be avoided by controlling the water to TEOS mole ratio alone or in combination with control of pH, addition of alcohol, or both.

A templated film is made by spin-coating the silica precursor solution. The solution is dispensed onto the surface of a substrate and spun using a spin-coater, for example at 2000 rpm for 30 seconds. The substrate is preferably a silicon wafer or an aluminum-coated silicon wafer, but it is not limited to these substrates.

The spin-coating technique used in the present invention requires no atmosphere control when used with these surfactant-containing solutions, and the method should be readily applicable to microelectronics manufacturing. The technique produces films with good thickness uniformity across wafers ranging from small to large surface area. Films

produced by the method of the present invention have film thickness from about 0.2 μm to about 1.5 μm with a thickness variation having a standard deviation of less than $\pm 5\%$. For example, one film with a thickness of about 0.8 μm had a thickness variation with a standard deviation of less than 25 nanometers (0.3%) across a 4-inch wafer. The film thickness can be controlled by adjusting the relative ratios of the solution compounds, and also by varying the spinning rate during deposition.

After spin-coating, the surfactant-templated film is formed into a hydroxylated mesoporous film by removal of the aqueous solvent, the acid, and the surfactant. Aqueous solvent removal is typically achieved by heating the spin-coated film. For example, exposing the spin-coated film to a temperature of 115°C for 1 hour completes drying and increases condensation of the silica. Further heat treatment (calcination) of the film, for example at a temperature of 475°C for 5 hours, or at 400°C on a hot plate for 5 minutes in N₂ gas, removes the surfactant and forms a mesoporous film that is partially hydroxylated.

The partially hydroxylated film is chemically dehydroxylated into a mesoporous silica film by exposing the partially hydroxylated film to a silicon-based organic compound such as a silane, either as the pure liquid or pure vapor or as a solution, or as a vapor in a carrier gas or gas mixture. The silane can be chosen from the following and not limited to trimethyl iodasilane, trimethyl chlorosilane, dimethyl dimethoxy silane, hexamethyl disilazane dimethyl dichlorosilane hexaphenyl disilazane, and diphenyl tetramethyl silazane. . Additionally, the silane exposed film may be further exposed to, a dehydroxylating gas or to a heat treatment. The silane treatment may be preceded and followed by a vacuum treatment or a treatment in an inert gas or forming gas, or both. The partially hydroxylated film is preferably dehydroxylated in a two-step process which includes a soak treatment in a solution of hexamethyl disilazane in an organic solvent and exposure to an H₂ in N₂ gas at an elevated temperature. The partially hydroxylated film is more preferably dehydroxylated in a multiple step high temperature process, which includes an initial vacuum treatment, followed by a vapor phase silane treatment, followed by a second vacuum treatment. The silane/vacuum treatment step is preferably repeated using the same silane or a different silane and is followed by a high temperature inert gas or forming gas treatment.

For example, soaking the hydroxylated film for 24 hours in a 10% solution of hexamethyl disilazane in toluene and then exposing it to 2% H₂ in N₂ gas at 400°C for 2 hours results in effective dehydroxylation of the mesoporous film, which then exhibits stable

dielectric properties in moist air. This sequence of dehydroxylation process steps is preferably repeated once. The resulting mesoporous film has a dielectric constant typically less than 2.5 under ambient humid conditions, and the dielectric constant of the film is stable in moist or humid atmosphere over long periods of time.

5

EXAMPLE 1

An experiment was conducted to demonstrate the efficacy of a preferred embodiment of the present invention. Three different surfactants in the polyoxyethylene ether family were investigated: (1) $C_{12}H_{25}(CH_2CH_2O)_{10}OH$, also known as $C_{12}EO_{10}$ or 10 lauryl ether; (2) 10 $C_{16}H_{33}(CH_2CH_2O)_{10}OH$, also known as $C_{16}EO_{10}$ or 10 cetyl ether; and (3) $C_{18}H_{37}(CH_2CH_2O)_{10}OH$, also known as $C_{18}EO_{10}$ or 10 stearyl ether. All the films with these surfactants were prepared using a solution with the following molar ratios:
TEOS:H₂O:ethanol:hydrochloric acid = 1 : 5 : 5 : 0.05.

The surfactant/TEOS mole ratio was varied from about 0.10 to about 0.50. All the components except for the TEOS were mixed until a homogeneous solution was obtained. When the surfactant/TEOS mole ratio is greater than about 0.2 and ratios of TEOS:H₂O:ethanol are about 1 : 5 : 5, homogeneity is more readily achieved by heating the solution from about 40 °C to about 50 °C, especially for polyoxyethylene ether surfactants. Heating may not be needed for more dilute solutions.

TEOS was then added and the solution was stirred. Following addition of TEOS, the solution was aged for 20 hours at room temperature. No precipitate was formed under these solution conditions.

The aged solution was dispensed onto the surface of polished 4-inch Si wafers by spin-coating at 2000 rpm for 30 seconds using a spin-coater.

The resulting surfactant-templated films were converted to a mesoporous film by removing the aqueous solvent, the acid, and the surfactant. This removal was achieved by subjecting the templated films to a temperature of 115°C for 1 hour. Complete removal of the surfactant from the films was achieved by calcination (heat treatment) at 475°C for 5 hours.

Prior to making electrical/capacitance measurements, the calcined films were characterized by nuclear reaction analysis (NRA) to determine porosity, and by profilometry to measure thickness. The NRA porosity data was not used as an exact measure of porosity,

but rather was used for guidance to help determine which films to select for further electrical/capacitance measurements.

FIG. 1 shows the porosity determined by NRA for the C_xEO_{10} polyoxyethylene ether surfactant series. The graph shows only porosity values using the different surfactants for only specific surfactant/TEOS values. For several higher surfactant/TEOS ratios the film quality was not acceptable for evaluation of electrical properties, and films formed with such ratios were therefore not investigated further. For consideration as dielectric films in semiconductor devices, the film thickness should be in the range of about 0.5 to about 1.2 μm . In addition, the films should be uniform in thickness, crack-free, and without major blemishes or surface defects. Films with non-wetted islands, cracks, ring-like structures, serrated patterns or cloudy inclusions were not considered for electrical evaluation. Defects such as comets (e.g. due to dust particles on the wafer) on otherwise uniform films were considered acceptable, as these could not be attributed to inherent solution properties. The table E1-1 lists the observations in terms of film quality with these surfactants at different concentrations.

Table E1-1: Film Quality for C_xEO_{10} based Films

Surfactant>>>> Surfactant/TEOS mole ratio (below)	Film Quality $C_{12}EO_{10}$	Film Quality $C_{16}EO_{10}$	Film Quality $C_{18}EO_{10}$
0.10	Good	Acceptable	Acceptable
0.17	Good	Poor	Poor
0.24	Poor	Acceptable	Poor
0.30	Poor	Acceptable	Poor
0.40	Poor	Poor	Poor
0.50	Poor	Poor	Poor

Based on the NRA porosity data shown in FIG. 1 and the observations concerning film quality, two films were selected for electrical measurements. These two films as shown in Table 1 were those prepared with solutions containing (1) $C_{12}EO_{10}$, surfactant/TEOS mole ratio of 0.17; and (2) $C_{16}EO_{10}$, surfactant/TEOS mole ratio of 0.30.

Initial electrical testing of these calcined films for capacitance using a precision LCR meter yielded dielectric constants (i.e. capacitance) much higher than expected for porous films, because the film still contained a significant amount of hydroxyl (-OH) groups.

Each of these two partially hydroxylated films was therefore dehydroxylated by exposing the hydroxylated film separately to a silane and a dehydroxylating gas. The films were dehydroxylated by treatments of soaking for 24 hours in a 10% solution of hexamethyl disilazane in toluene and exposure for 2 hours to 2% H₂ in N₂ gas at 400°C. This sequence of dehydroxylation process steps was repeated once on each film, and the dielectric constant was measured after each of these steps.

The capacitance measurements were performed as follows. The backside of the wafer was scratched/etched to expose bare silicon surface and a layer of gold was then sputter-deposited. On the top film side, an array of gold dots approximately 2.8 mm in diameter was formed by sputtering using a shadow mask. Capacitance was measured at room temperature at ambient conditions for four dots on each sample, and the dielectric constant was calculated using the film thickness and dot diameter. The dielectric constant data obtained in this way is shown in FIG. 2 and FIG. 3 for the two different films.

The data in FIG. 2 shows that a dielectric constant of 1.80 can be obtained for the film synthesized with the C₁₂EO₁₀ surfactant. The data in FIG. 3 shows that a dielectric constant of 1.85 can be obtained for the film synthesized with the C₁₆EO₁₀ surfactant. Such low dielectric constants indicate tremendous promise for application of such mesoporous silica films prepared with small polyoxyethylene ether surfactants in semiconductor devices. The low dielectric constants obtained with these films are also relatively stable, increasing by less than 5% over a period of one day in ambient laboratory conditions with temperatures at 20-22°C and a relative humidity of 40-65%. The dielectric constants did not increase in value thereafter.

The pore structure of the surfactant templated mesoporous film was probed by low angle x-ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD spectra of the film on the wafer for two different directions, radial and tangential, are shown in FIGS 4A, 4B. The spectra did not contain any peak in the range of 2 to 6 degrees 2-theta, thereby indicating that pores are not ordered. A TEM micrograph of a section of the film in FIG. 5 indicates that the pores are disordered with an isotropic nanoporous structure. Pore sizes were estimated to be less than 3 nm from TEM micrographs, and from nitrogen adsorption/desorption analysis of powders prepared from the solution by a rapid spray drying process.

Film planarity and surface topography were measured by optical profilometry. Minimal striation-type surface texture was observed in these films. A surface contour map of the film is shown in FIG. 6a. Roughness is generally less than ± 50 angstroms over length scales of tens of microns (FIG. 6b).

5 The elastic modulus of the mesoporous silica film was measured with a Hysitron Picoindenter™ using a Berkowich diamond tip. The instrument and tip were calibrated on a dense silica standard with a modulus of 70 GPa. A range of indentation loads (50-300 μ N) and residence time (50-900 s) at maximum load were studied. For the measurement parameters used, indentation depths were less than 10% of the film thickness, and therefore
10 substrate effects were not expected to affect the measured values. The effect of indentation load on measured modulus values for a residence time of 300 s is shown in FIG. 7 for the mesoporous silica film. The modulus is in the range of 14-17 GPa for a highly porous film prepared with the $C_{12}EO_{10}$ polyoxyethylene ether surfactant with a porosity of $\approx 55\%$. The relative modulus of the porous silica film with respect to dense silica is in reasonable
15 agreement with calculations for porous solids based on either closed or open porosity. The relatively high modulus for the porous film indicates promise for withstanding CMP in interconnect fabrication.

EXAMPLE 2

20 An experiment was conducted to demonstrate use of various polyoxethelene ether surfactants alone and in combination in preparation of a mesoporous silica film with low dielectric constants. The components of the spin coating solutions including the surfactant type and amount used in each solution, as well as the dielectric constant of selected films are shown in Table E2-1. All the components except for the TEOS were mixed until a
25 homogeneous solution was obtained. In this experiment, the components were added in the following order: surfactant, ethanol, water and acid. When the surfactant was a solid at room temperature, the surfactant was heated to about 30 to 40°C to melt the surfactant, before adding other solution components. Heating the surfactant is not always necessary, but a homogeneous solution could be more readily obtained by this procedure. TEOS was then
30 added and the solution was stirred. Following addition of TEOS, the solution was aged for 20 hours at room temperature and dispensed onto the surface of polished 4-inch Si wafers by spin-coating at 2000 rpm for 30 seconds using a spin-coater.

The resulting surfactant-templated films were converted to mesoporous film by heating on a series of three hot plates. The highest hot plate temperature was about 400 °C. Selected films from this set were subjected to a dehydroxylation procedure including treatment in hexamethyl disilazane solution followed by treatment in 2% H₂/N₂ as described previously, and the film dielectric constants measured. The table shows that film dielectric constants of less than 2.25 can be obtained using more than one surfactant.

TABLE E2-1

Sample	Composition: Mole Ratio								
#	Teos	H ₂ O	ETOH	HNO ₃	Surfactant 1		Surfactant 2		k'
CC24	1	5	10	0.05	0.1	C ₁₂ EO ₁₀	0.1	C ₁₆ EO ₁₀	
CC25	1	5	10	0.05	0.13	C ₁₂ EO ₁₀	0.13	C ₁₆ EO ₁₀	
CC26	1	5	10	0.05	0.15	C ₁₂ EO ₁₀	0.15	C ₁₆ EO ₁₀	2.16
CC27	1	5	5	0.05	0.06	C ₁₂ EO ₁₀	0.06	C ₁₈ EO ₂₀	
CC28	1	5	5	0.05	0.1	C ₁₂ EO ₁₀	0.1	C ₁₈ EO ₂₀	2.11
CC29	1	5	5	0.05	0.1	C ₁₂ EO ₁₀	0.1	C ₁₂ EO ₄	
CC30	1	5	5	0.05	0.13	C ₁₂ EO ₁₀	0.13	C ₁₂ EO ₄	
CC31	1	5	5	0.05	0.15	C ₁₂ EO ₁₀	0.15	C ₁₂ EO ₄	2.23

EXAMPLE 3

The disordered pore structures of films prepared with polyoxethelene ether surfactants were probed more extensively by low angle x-ray diffraction to determine any characteristic features in the x-ray spectra of these films. The components of the spin coating solutions including the surfactant type and amount used in each solution are shown in Table E3-1. All the components except for the TEOS were mixed until a homogeneous solution was obtained. In this experiment, the components were added in the following order: surfactant, ethanol, water and acid. When the surfactant was a solid at room temperature, the surfactant was heated to about 30 to 40°C to melt the surfactant, before adding other solution components. Heating the surfactant is not always necessary, but a homogeneous solution could be more readily obtained by this procedure. TEOS was then added and the solution was stirred. Following addition of TEOS, the solution was aged for 20 hours at room temperature and dispensed onto the surface of polished 4-inch Si wafers by spin-coating at 2000 rpm for 30 seconds using a spin-coater.

Table E3-1

Composition: Mole Ratios						
Sample #	TEOS	H ₂ O	EtOH	HCl	HNO ₃	Surfactant
144-3-I-D	1	5	5	0.05		0.19 C ₁₂ EO ₁₀
CC22C	1	5	10		0.05	0.3 C ₁₂ EO ₁₀
CC29A	1	5	5		0.05	0.1 C ₁₂ EO ₁₀ 0.1 C ₁₂ EO ₄
CC81-1B	1	5	20	0.05		0.2 C ₁₆ EO ₁₀
CC83-1B	1	5	20	0.05		0.2 C ₁₈ EO ₁₀

The resulting surfactant-templated films were converted to mesoporous films by heating on a series of three hot plates. The highest hot plate temperature was about 400 °C.

- 5 Two films from this set, 143-3-I-D and CC22C were subjected to a dehydroxylation procedure including a treatment in hexamethyl disilazane solution followed by treatment in 2% H₂/N₂ as described previously.

The films were probed by x-ray diffraction, using the experimental parameters below. X-ray spectra were obtained on a scanned area about 1 cm x 1 cm in extent, with the centroid
10 of the scanned area being located about 3.5 cm from the center of the wafer. Spectra were obtained in both the radial and tangential directions of the x-ray beam with respect to the circular wafer.

Scan Range: 1.00 - 6.00 deg (2Theta)

15

Scan Rate: 0.05 deg / 10 sec

Scan Type: Continuous (i.e., not Step-Scan)

20 Diffractometer: Philips X'Pert MPD (Model PW3040/00)

X-ray Source: Sealed Ceramic Tube, Long-Fine Focus (LFF) Cu Anode (Cu K alpha radiation)

X-ray Power: 40 kV, 50 mA (2000 W)

Goniometer Radius: 250 mm.

5 Incident Beam Optics:

- 0.04 rad Soller Slit
- Programmable, Automatic Divergence Slit (10 mm spot length)
- 10 mm Beam Mask (10 mm spot width)

10 Receiving Optics:

- 0.04 rad Soller Slit
- Programmable, Automatic Anti-Scatter Slit (10 mm spot length)
- Programmable Receiving Slit (0.2 mm)
- Curved Graphite Monochromator

15

Detector: Xe Proportional Counter

144-3-I-D: X-ray spectra corresponding to the radial and tangential directions are shown in FIG. 8a, FIG. 8b respectively. The intensity of the diffracted or reflected beam steadily increases as lower angles are approached, because a greater percentage of the direct beam reaches the detector, in spite of careful alignment of the system components and control of the sample height relative to the path of the incident and reflected beam. In spite of this increasing intensity, there is evidence of a peak near 1.1 degrees 2-theta in both spectra. Transmission electron microscopy of a thin section of this film showed no evidence of ordered porosity. The areas of the film that were studied did not show any regular geometric arrangement of pores, especially long-range geometric arrangement.

CC22C: X-ray spectra corresponding to the radial and tangential directions are shown in FIG. 9a, FIG. 9b respectively. In the tangential directions, there is evidence of a peak at about 1.1 degrees, but in the radial direction, a clear peak is not evident. Only increasing intensity with lower angles is observed.

CC29C: X-ray spectra corresponding to the radial and tangential directions are shown in FIG. 10a, FIG. 10b respectively. In both the radial and the tangential directions, there is evidence of a peak at about 1.1 to 1.2 degrees 2-theta.

CC81-1B: X-ray spectra corresponding to the radial and tangential directions are shown in FIG. 11a, FIG. 11b respectively. In both the radial and the tangential directions, there is evidence of a peak at about 1.1 to 1.2 degrees 2-theta.

CC83-1B: Two sets of x-ray spectra obtained on this sample are shown in FIGS. 12a – 12d. One set (radial and tangential direction) was obtained about a quarter-wafer away (about 90 degrees rotation of the wafer) from the other. In FIGS. 12a, 12b, the spectra obtained in the radial and tangential direction in one area do not show clear evidence of a peak at low angles. However, each of the spectra in FIGS. 12c, 12d from the other area on the sample contains a single peak at around 1.1-1.2 degrees 2-theta. Transmission electron microscopy of a thin section of this film showed no evidence of ordered porosity. The areas of the film that were studied did not show any regular geometric arrangement of pores, especially long-range geometric arrangement.

The observations concerning x-ray reflections at low angle and transmission electron microscopy in this example, in combination with the observations concerning x-ray reflections and the microstructure by TEM in Example 1 are consistent with a pore structure that does not have any ordered geometric "crystalline" arrangement, especially long range. This disordered porosity was characterized by an X-ray diffraction peak at very low angles (about 0.75 to about 2 degrees 2- theta). It is to be noted that this peak is not observed 100% of the time for disordered porosity.

EXAMPLE 4

Dehydroxylation of mesoporous silica films utilizing a silane in the vapor form at room temperature can produce dielectric constants less than 2.5. A mesoporous film on a silicon wafer was placed in a stainless steel reaction vessel having an internal volume of ~ 0.081 cm³. The reaction vessel (equipped with inlet and outlet high temperature valves) was connected to a high vacuum line via vacuum tubing. The reactor was placed in a sand bath and temperatures were monitored employing thermocouples deployed uniformly about the reactor. The initial heating up step (0 min. to 2 hrs) was conducted with the chamber placed under high vacuum (~10⁻⁵ torr). After the reaction chamber had achieved the desired

temperature it was opened to the silane in vapor phase. The pressure of the silane vapor was dependent on the silane's vapor pressure at or near its boiling point. After the desired time had elapsed the chamber was placed under vacuum. The treatments of the mesoporous films essentially consisted of a vacuum treatment followed by one or more silane treatments in

5 vapor phase followed by one or more vacuum treatments at temperatures ranging from 298 to 723K (25C to 450C). Vacuum treatments and silane treatments were varied in duration from 5 minutes to 2 hours. This procedure was repeated for a number of cycles for the samples illustrated in Table E4-1. Upon cooling, the wafer was removed from the reaction vessel and, following deposition of gold electrodes on the surfaces, was placed in a tube furnace and

10 treated with forming gas (2% H_2/N_2) at 673K (400C) for two hours. The capacitance of the film was measured under ambient conditions. The films were also placed in a flow of dry nitrogen gas and film capacitance measured. Finally the wafer was placed in a sealed glass container containing a beaker of water to simulate 100% relative humidity for time periods ranging from 1 to 3 days, and the sample then was removed and the capacitance measured

15 again in room air. Several different silanes were investigated, including trimethyl iodosilane, trimethyl chlorosilane, dimethyl dimethoxy silane, and hexamethyl disilazane. The results of experiments with trimethyl iodosilane and hexamethyl disilazane are set forth in Table E4-1. These results illustrate that, depending on the silane and the treatment conditions employed, low dielectric constants (<2.5) on mesoporous silica films can be achieved with a procedure

20 that includes an exposure of the mesoporous silica film to silane. This exposure may occur in high humidity conditions. These results indicate that dehydroxylation by silanes may be most effective with a procedure that includes removal of gas-phase or physisorbed species in the porous film before and/or after the silane treatment step. This removal of gas-phase or physisorbed species was carried out by treatment in vacuum or by treatment in flowing

25 forming gas, but may also be accomplished by treatment in other flowing inert gases such as high purity nitrogen or argon.

TABLE E4-1

Sample #	Silane (pressure in torr)	Total Mmol e silane	Temp. °C	Time * (min)	Number of cycles (silane treatment)	K' (in air)	K' (in flowing nitrogen)	K' (in air, after 100% humidity)**
JB-3	(CH ₃) ₃ SiI 36 torr	0.16	275	60	1	1.66	1.57	1.91
JB-6	CH ₃) ₃ SiI 30 torr	0.17	400	10	3	1.73	1.65	1.72
JB-8	HMDS** * 19 torr	0.17	350	10	5	1.77	1.67	1.86

*Silane treatment time, in minutes. Generally, vacuum time is the same.

**Exposure to 100% humidity for ~15 hours, capacitance immediately measured thereafter in ambient air.

***Hexamethyl disilazane

It is believed that such treatment may be best accomplished in a chamber wherein the film temperature can be controlled, and where the required gases can be fed into the chamber in the proper sequence, and the chamber pumped down in vacuum before and/or after silane exposure. We designed an experimental reaction chamber to be used for dehydroxylation of mesoporous silica films supported on silicon wafers which could be an independent chamber or part of an integrated spin-track tool. The stainless steel chamber is constructed to hold 4, 6, 8 and 12 inch wafers. Under high vacuum the chamber will support an outer pressure of one atmosphere, and the cooled seal on the front-opening door will maintain a vacuum of 10⁻⁵ torr. The internal self-heating shelves will heat to 500C, and internal circulation is assured with a fan. After an initial vacuum treatment, a gaseous silane is pumped into the chamber at the desired pressure, and thereafter a vacuum is again applied. The cycle may be repeated as many times as necessary to achieve the desired degree of dehydroxylation. After the last vacuum treatment, forming or an inert gas is pumped into the chamber.

EXAMPLE 5

Mono- and di-alkyl substituted alkoxysilanes can be used as additional silica precursors in the surfactant-containing spin coating solution used to prepare low dielectric

constant mesoporous silica films with dielectric constants of <2.5 . A series of solutions were prepared as described in example 1 except that methyl triethoxysilane and dimethyl dimethoxysilane were added to the one mole ratio of tetraethoxysilane. Molar ratios of 0.95 : 0.05 to 0.25 : 0.75 of TEOS to the alkyl-ethoxysilane respectively were prepared. The surfactant used was 10 lauryl ether. The surfactant to silica precursor mole ratio was 0.17. Silicon wafers were spin coated with these solutions and heat-treated as described in example 2. Selected coated wafers were subjected to the dehydroxylation treatment as follows. The coated silicon wafer was placed in a stainless steel reaction vessel having an internal volume of $\sim 0.081 \text{ cm}^3$. The reaction vessel (equipped with inlet and outlet high temperature valves) was connected to a high vacuum line via vacuum tubing. The reactor was placed in a sand bath and temperatures were monitored employing thermocouples deployed uniformly about the reactor. The initial heating up step (0 min. to 2 hrs) was conducted with the chamber placed under high vacuum ($\sim 10^{-5}$ torr). After the reaction chamber had achieved the desired temperature it was opened to the silane in vapor phase. The pressure of the silane vapor was dependent on the silane's vapor pressure at or near its boiling point. After the desired time had elapsed the chamber was placed under vacuum. The treatments of the mesoporous films essentially consisted of a vacuum treatment followed by one or more silane treatments in vapor phase followed by one or more vacuum treatments at temperatures ranging from 298 to 723K (25C to 450C). Vacuum treatments and silane treatments were varied in duration from 5 minutes to 2 hours. Upon cooling, the wafer was removed from the reaction vessel and gold electrodes deposited on the surfaces. The capacitance of the film was measured under ambient conditions. The films were also placed in a flow of dry nitrogen gas and film capacitance measured. The results of one wafer are given in Table E5-1.

TABLE E5-1

Sample #	Siloxane molar ratio	Dehydroxylation silane (pressure)	Total mmol silane	Time (min)	Temp (°C)	No. of cycles	K' Air	K' nitrogen
JB-21	0.85 TEOS 0.15 Methyl triethoxide	(CH ₃) ₃ SiH 17 torr	0.23	10	390	5	2.24	2.23

The present invention further involves improvements to the two-step method of dehydroxylating a silica surface that is hydroxylated. The basic two-step method of dehydroxylation has the steps of exposing the silica surface separately (1) to a silicon organic compound and (2) to a dehydroxylating gas.

The improvements of the present invention are (a) repeating the basic two-step method and achieving a dielectric constant less than 2.25; (b) using an inert gas substantially free of hydrogen as the dehydroxylating gas and achieving a safer dehydroxylation method; (c) combining the two-step method with surfactant templating method of making mesoporous films, and (d) combinations thereof.

A hydroxylated film is dehydroxylated by exposing the hydroxylated film separately to a silicon organic compound, preferably a silane, and to a dehydroxylating gas. The exposure to a silane may be as a silane vapor, silane liquid, silane solution or combination thereof. In a silane solution, the solvent is preferably non-aqueous, for example toluene. The silane may be trimethylchlorosilane, hexamethyl disilazane or combinations thereof. The exposure to the dehydroxylating gas is preferably at an elevated temperature. The dehydroxylating gas may be an inert gas or a mixture of an inert gas containing hydrogen. The inert gas is substantially free of hydrogen which is defined herein as either having no hydrogen or an amount of hydrogen that is ineffective in the dehydroxylation. An amount of hydrogen below detectable limits is practically ineffective for the dehydroxylation.

Dehydroxylation of polyoxyethylene ether surfactant-based films is a preferred embodiment. However, lower dielectric constants by such dehydroxylation procedures are also obtainable on films prepared with other surfactants including but not limited to ammonium (CTAC) surfactant-based films.

EXAMPLE 6

In the examples reported here, $C_{12}H_{25}(CH_2CH_2O)_{10}OH$ (also known as $C_{12}EO_{10}$ or 10 lauryl ether) was used as the surfactant to introduce porosity in the film. Data was also
5 obtained on films prepared with another surfactant, $C_{16}H_{33}(CH_2CH_2O)_{10}OH$ (also known as $C_{16}EO_{10}$ or 10 cetyl ether) of the same family using some of the dehydroxylation treatments reported below.

All the films were prepared using a solution with the following molar ratios:
TEOS:H₂O:ethanol:hydrochloric acid = 1 : 5 : 5 : 0.05. The surfactant/TEOS mole ratio was
10 0.17. All the components except for the TEOS were mixed until a clear homogeneous solution was obtained, and then TEOS was added and the solution was stirred. Following addition of TEOS, the solution was aged for ~20 h at room temperature and then spin-coated on polished 4-inch Si wafers. After spin-coating, the film was then kept at 115°C for at least 1 hour to complete drying and increase condensation of the silica, and was later calcined at
15 475°C for 5 hours.

The calcined films were subjected to one or more of the following dehydroxylation treatments:

a) immersed in 10% solution of HMDS in toluene for 20-24 hours, and then
20 sonicated in isopropyl alcohol and dried in flowing nitrogen at room temperature. This procedure is hereafter referred to as "HMDS (L)"

b) heat treated at 400°C for 2 hours in flowing 2%H₂-98%N₂ gas. This procedure hereafter referred to as "2%H₂"

c) heat treated at 400°C for 2 hours in flowing argon. This procedure hereafter
25 referred to as "Ar"

d) film flooded with pure HMDS for 15 seconds, spun to 2000 rpm, and then film flooded with isopropyl alcohol for 15 seconds, and then spun at 2000 rpm.

The capacitance measurement was performed as follows. After film deposition and treatment, the backside of the wafer was scratched/etched to expose bare silicon surface and a
30 layer of gold was then sputter-deposited. On the top film side, an array of gold dots approximately 2.8 mm in diameter was formed by sputtering using a shadow mask.

Capacitance was measured for four dots on each sample, and the dielectric constant calculated using the film thickness and dot diameter.

The average dielectric constants obtained in this manner are shown in Table E6-1. For some of the samples that received a final heat treatment in hydrogen-containing gas or argon, the samples were first electroded with gold prior to the final heat treatment. The capacitance was measured before and after the heat treatment. Table E6-1 also lists contact angle of water droplets on films after some treatments.

Table E6-1

10. **Effect of Dehydroxylation Treatment on Dielectric Constant of Mesoporous Silica Films Prepared with C₁₂EO₁₀ Polyoxyethylene Ether Surfactant**

Description of Dehydroxylation Procedure	Sample ID	Water Contact Angle – "Measure of Hydrophobicity"	Dielectric Constant
2%H ₂	103-2-1-B1	12°	2.67
HMDS (L)	XL-92-2		3.34
HMDS (L)>>2%H ₂	XL-92-2		2.41
HMDS(L)>>2%H ₂ >>HMDS(L)	103-2-1-A1 112-1-III-D1	75°	2.14 2.56
HMDS(L)>>2%H ₂ >>HMDS(L)>>2%H ₂	103-2-1-A2 112-1-III-D1	72°	1.74 2.12
HMDS(L)>>Ar	103-2-1-B2	42°	1.95
HMDS(L)>>Ar>>HMDS(L)	112-1-III-D2		2.55
HMDS(L)>>Ar>>HMDS(L)>>Ar	112-1-III-D2		2.24
HMDS spin coat>>2%H ₂ >>HMDS spin coat	103-2-1-C1		2.48
HMDS spin coat>>2%H ₂ >>HMDS spin coat>>2%H ₂	103-2-1-C1		2.10

15 From the data in Table E6-1, two conclusions can be drawn. First, compared to untreated silica films, all the treatments result in low dielectric constants in the film. Second, dielectric constants of ~2.50 can be obtained after treatment in the silane solution followed by treatment in an inert gas or a hydrogen-containing gas at moderately elevated temperatures. In one film (103-2-1A2), a dielectric constant as low as 1.74 was obtained after two treatments in the silane and two treatments in 2%H₂/N₂. In another film (103-2-1-B2), a

dielectric constant as low as 1.95 was obtained with only a single treatment in the silane solution and one treatment in argon.

For many of the samples listed in Table E6-1, capacitance was also measured as a function of time either immediately after sputter-deposition of the gold electrodes, or immediately after the electroded sample was removed from the furnace after the final heat treatment.

The dielectric constant as a function of aging time for times up to 2-3 days is shown in FIG. 13. Except for the film that received only a treatment in 2% H_2 at 400°C (film #103-2-1-B1), all samples showed excellent stability in capacitance (dielectric constant) with time at room temperature. The ambient relative humidity during the aging measurements was ~40-65%. The low dielectric constants obtained with the films that received treatment(s) in HMDS solution and exposure to dehydroxylating gas heated to about 400°C are also very stable over very long times, increasing by less than 5% over a week in ambient laboratory conditions with temperature at 20-22°C and relative humidity of 40-65%. Small changes in the dielectric constant in this aging study appear to correlate well with humidity changes during the experiment. For example, capacitance measured at the highest humidity values was slightly higher than capacitance measured at the lowest humidity values in the experiment.

CLOSURE

While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

CLAIMS

1. A mesoporous silica film prepared from a surfactant containing solution, having a dielectric constant less than 3 that has both a relative stability and an absolute stability in a humid atmosphere, a film thickness from about 0.1 μm to about 1.5 μm , and an average pore diameter less than or equal to about 20 nm.

2. The mesoporous silica film as recited in claim 1, wherein said average pore diameter is less than or equal to about 10 nm.

3. The mesoporous silica film as recited in claim 1, wherein said thickness has a standard deviation less than $\pm 5\%$.

4. The mesoporous silica film as recited in claim 1, wherein a porosity of said mesoporous silica film is disordered.

5. A mesoporous silica film having a thickness from about 0.1 μm to about 1.5 μm and a standard deviation about said thickness, wherein said standard deviation is less than $\pm 5\%$.

6. The mesoporous silica film as recited in claim 5, wherein a dielectric constant of said mesoporous silica film is less than 3.

7. The mesoporous silica film as recited in claim 5, having a dielectric constant with a relative stability and an absolute stability.

8. The mesoporous silica film as recited in claim 5, having an average pore size less than or equal to about 20 nm.

9. The mesoporous silica film as recited in claim 5, having a porosity that is disordered.

10. A mesoporous silica film prepared from a surfactant containing solution, comprising a porosity that is disordered, said porosity having an average pore diameter of less than or equal to about 20 nm, and a film thickness from about 0.1 μm to about 1.5 μm .

11. The mesoporous silica film as recited in claim 10, having a dielectric constant less than 3, said dielectric constant having both a relative stability and an absolute stability.

12. A method of making a mesoporous film comprising the steps of:

- (a) combining a silica precursor with an aqueous solvent, a catalyst and a surfactant into a precursor solution;
- (b) spin coating said precursor solution into a templated film;
- (c) removing said aqueous solvent, said catalyst and said surfactant from said templated film and forming a hydroxylated film with disordered porosity; and
- (d) dehydroxylating said hydroxylated film and obtaining said mesoporous film.

13. The method as recited in claim 12, wherein said surfactant is a polyoxyethylene ether surfactant.

14. The method as recited in claim 13, wherein said polyoxyethylene ether surfactant is $\text{C}_{12}\text{H}_{25}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{OH}$ also known as $\text{C}_{12}\text{EO}_{10}$ or 10 lauryl ether; $\text{C}_{16}\text{H}_{33}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{OH}$ also known as $\text{C}_{16}\text{EO}_{10}$ or 10 cetyl ether; $\text{C}_{18}\text{H}_{37}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{OH}$ also known as $\text{C}_{18}\text{EO}_{10}$ or 10 stearyl ether; $\text{C}_{12}\text{H}_{25}(\text{CH}_2\text{CH}_2\text{O})_4\text{OH}$ also known as C_{12}EO_4 or 4 lauryl ether; $\text{C}_{16}\text{H}_{33}(\text{CH}_2\text{CH}_2\text{O})_2\text{OH}$ also known as C_{16}EO_2 or 2 cetyl ether or combinations thereof.

15. The method as recited in claim 12, wherein said surfactant is in combination with a chemical agent selected from the group of a second surfactant, smaller hydrophilic molecular compounds, and with organic co-solvents.

16. The method as recited in claim 15, wherein said second surfactant is selected from the group consisting of non-ionic surfactant, cationic surfactant, anionic surfactant, amphoteric surfactant and combinations thereof.

17. The method as recited in claim 16, wherein said cationic surfactant is an ammonium-based surfactant.

5 18. The method as recited in claim 15, wherein said smaller hydrophilic molecular compounds are selected from the group consisting of glycerol, propylene glycol, and ethylene glycol.

10 19. The method as recited in claim 15, wherein said organic co-solvents are selected from the group consisting of mesitylene, octane and combinations thereof.

15 20. The method as recited in claim 12, wherein said silica precursor is selected from the group consisting of tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate (TMOS), methyl triethoxysilane, phenyl triethoxy silane, dimethyl dimethoxy silane ethyl triethoxysilane, and combinations thereof.

21. The method as recited in claim 12, wherein said aqueous solvent comprises ethanol and water.

20 22. The method as recited in claim 12, wherein said acid is selected from the group consisting of inorganic acid, organic acid and combinations thereof.

25 23. The method as recited in claim 12, wherein said precursor solution includes at least one other surfactant.

24. The method as recited in claim 12, wherein said precursor solution includes at least one smaller hydrophilic molecular compound.

30 25. The method as recited in claim 12 wherein said precursor solution includes at least one organic co-solvent.

26. The method as recited in claim 23, wherein said at least one other surfactant is selected from the group consisting of non-ionic surfactant, cationic surfactant, anionic surfactant, amphoteric surfactant and combinations thereof.

5 27. The method as recited in claim 24, wherein said at least one smaller hydrophilic molecular compound is selected from the group consisting of glycerol, propylene glycol, ethylene glycol and combinations thereof.

10 28. The method as recited in claim 25, wherein said at least one organic co-solvent is selected from the group consisting of mesitylene, octane and combinations thereof.

29. The method as recited in claim 12, wherein dehydroxylating occurs in the presence of a silicon-based organic compound in the vapor phase.

15 30. The method as recited in claim 29, wherein the silicon-based organic compound is a silane.

20 31. The method as recited in claim 30, wherein the silane is selected from the group consisting of trimethyl iodasilane, trimethyl chlorosilane, dimethyl dimethoxy silane, dimethyl dichloro silane, hexaphenyl disilazane, diphenyl tetramethyl silazane and hexamethyl disilazane .

25 32. A method of making a mesoporous film with a surfactant containing solution, the method comprising the steps of:

(a) combining a silica precursor with an aqueous solvent, a catalyst and a surfactant that is a polyoxethylene ether surfactant into a precursor solution;

(b) spin coating said precursor solution into a templated film;

(c) removing said aqueous solvent, said catalyst and said surfactant forming a
30 hydroxylated film having porosity; and

(d) dehydroxylating said hydroxylated film and obtaining said mesoporous film.

33. The method as recited in claim 32, wherein said polyoxyethylene ether surfactant is $C_{12}H_{25}(CH_2CH_2O)_{10}OH$ also known as $C_{12}EO_{10}$ or 10 lauryl ether; $C_{16}H_{33}(CH_2CH_2O)_{10}OH$ also known as $C_{16}EO_{10}$ or 10 cetyl ether; $C_{18}H_{37}(CH_2CH_2O)_{10}OH$ also known as $C_{18}EO_{10}$ or 10 stearyl ether; $C_{12}H_{25}(CH_2CH_2O)_4OH$ also known as $C_{12}EO_4$ or 4 lauryl ether; $C_{16}H_{33}(CH_2CH_2O)_2OH$ also known as $C_{16}EO_2$ or 2 cetyl ether or combinations thereof.

34. The method as recited in claim 32, wherein said porosity is disordered as indicated by an absence of an x-ray diffraction peak in the range of 2 to 6 degrees 2-theta.

35. The method as recited in claim 32, wherein said porosity is disordered, lacking a regular geometric arrangement of pores, and the pore structure is characterized by an x-ray diffraction peak between about 0.75 and about 2 degrees 2-theta.

36. The method as recited in claim 32, wherein said precursor solution includes at least one other surfactant.

37. The method as recited in claim 32, wherein said precursor solution includes at least one smaller hydrophilic molecular compound.

38. The method as recited in claim 32, wherein said precursor solution includes at least one organic co-solvent.

39. The method as recited in claim 32, wherein said precursor solution includes an agent selected from the group consisting of a second surfactant, a smaller hydrophilic molecular compound, an organic co-solvent and combinations thereof.

40. The method as recited in claim 36, wherein said at least one other surfactant is selected from the group consisting of non-ionic surfactant, cationic surfactant, anionic surfactant, amphoteric surfactant and combinations thereof.

41. The method as recited in claim 37, wherein said at least one smaller hydrophilic molecular compound is selected from the group consisting of glycerol, propylene glycol, ethylene glycol and combinations thereof.

5 42. The method as recited in claim 38, wherein said at least one organic co-solvent is selected from the group consisting of mesitylene, octane and combinations thereof.

43. The method as recited in claim 39, wherein said second surfactant is selected from the group consisting of non-ionic surfactant, cationic surfactant, anionic surfactant,
10 amphoteric surfactant and combinations thereof.

44. The method as recited in claim 39, wherein said smaller hydrophilic molecular compound is selected from the group consisting of glycerol, propylene glycol, ethylene glycol and combinations thereof.

15 45. The method as recited in claim 39, wherein said organic co-solvent is selected from the group consisting of mesitylene, octane and combinations thereof.

46. The method as recited in claim 32 wherein said silica precursor is selected
20 from the group consisting of tetraethyl orthosilicate (TEOS), tetramethyl orthosilicate, methyl triethoxysilane, phenyl triethoxy silane, dimethyl dimethoxy silane and combinations thereof.

47. The method as recited in claim 32 wherein said aqueous solvent includes ethanol.

25 48. The method as recited in claim 32, wherein said catalyst is selected from the group consisting of inorganic acid, organic acid and combinations thereof.

49. The method as recited in claim 48, wherein said organic acid is
30 carboxylic acid selected from the group consisting of methanoic acid (formic acid), ethanoic acid (acetic acid), ethandioic acid (oxalic acid), butanoic acid (butyric acid), and combinations thereof.

50. The method as recited in claim 32, wherein dehydroxylating occurs in the presence of a silicon-based organic compound in the vapor phase.

5 51. The method as recited in claim 50, wherein the silicon-based organic compound is a silane.

52. The method as recited in Claim 51, wherein the silane is selected from the group consisting of trimethyl iodosilane, trimethyl chlorosilane, dimethyl dichloro
10 silane, hexaphenyl disilazane, diphenyl tetramethyl silazane and hexamethyl disilazane.

53. A mesoporous silica film made by the method of claim 32, comprising:
a disordered porosity, lacking a regular geometric arrangement of pores, and
characterized by an x-ray diffraction peak between about 0.75 and about 2 degrees 2-theta;
15 a dielectric constant less than 3.0 that is stable;
a film thickness from about 0.1 μm to about 1.5 μm ; and
an average pore diameter less than or equal to about 20 nm.

54. A mesoporous silica film made by the method of claim 32, comprising:
20 a disordered porosity as indicated by an absence of an XRD peak in the range from 2
to 6 degrees 2-theta;
a dielectric constant less than 3.0 that is stable;
a film thickness from about 0.1 μm to about 1.5 μm ; and
an average pore diameter less than or equal to about 20 nm.

25 55. A mesoporous film made by the method of claim 12, comprising:
a dielectric constant less than 3.0 that is stable;
a film thickness from about 0.1 μm to about 1.5 μm ; and
an average pore diameter less than or equal to about 20 nm.

30 56. A method of making a mesoporous film comprising the steps of:
(a) combining a silica precursor with an aqueous solvent, an acid and a

polyoxethylene ether surfactant into a precursor solution;

(b) spin-coating said precursor solution into a templated film;

(c) removing said aqueous solvent, said acid and said surfactant forming a hydroxylated film; and

(d) dehydroxylating said hydroxylated film and obtaining said mesoporous film.

57. The method as recited in claim 56, wherein said polyoxyethylene ether surfactant is $C_{12}H_{25}(CH_2CH_2O)_{10}OH$ also known as $C_{12}EO_{10}$ or 10 lauryl ether; $C_{16}H_{33}(CH_2CH_2O)_{10}OH$ also known as $C_{16}EO_{10}$ or 10 cetyl ether; $C_{18}H_{37}(CH_2CH_2O)_{10}OH$ also known as $C_{18}EO_{10}$ or 10 stearyl ether; $C_{12}H_{25}(CH_2CH_2O)_4OH$ also known as $C_{12}EO_4$ or 4 lauryl ether; $C_{16}H_{33}(CH_2CH_2O)_2OH$ also known as $C_{16}EO_2$ or 2 cetyl ether or combinations thereof.

58. The method as recited in claim 57, wherein said polyoxyethylene ether surfactant is in combination with other small surfactants, with smaller hydrophilic molecules, and with organic co-solvents.

59. The method as recited in claim 58, wherein said small surfactants are ammonium-based surfactants.

60. The method as recited in claim 59, wherein said ammonium-based surfactants are cetyl trimethyl ammonium chloride.

61. The method as recited in claim 58, wherein said smaller hydrophilic molecules are selected from the group consisting of glycerol, propylene glycol, and ethylene glycol.

62. The method as recited in claim 58, wherein said organic co-solvents are selected from the group consisting of mesitylene and octane.

63. The method as recited in claim 56, wherein said silica precursor is tetraethyl orthosilicate (TEOS).

64. The method as recited in claim 56, wherein said aqueous solvent comprises ethanol and water.

5 65. The method as recited in claim 56, wherein said acid is hydrochloric acid.

66. A mesoporous film having a dielectric constant less than 2.5, a film thickness from about 0.2 μm to about 1.5 μm , and an average pore diameter less than or equal to about 5 nm.

10 67. A mesoporous film having a thickness from about 0.2 μm to about 1.5 μm and a standard deviation about said thickness that is less than +/- 5%.

68. A mesoporous silica film prepared from a surfactant containing solution,
15 having a dielectric constant less than 3 that has both a relative stability and an absolute stability in a humid atmosphere, a film thickness from about 0.1 μm to about 1.5 μm , an average pore diameter less than or equal to about 20 nm, and a porosity that is disordered.

69. The mesoporous silica film as recited in claim 68, wherein disordered is
20 indicated by the absence of an X-ray diffraction peak in the range of about 2 to about 6 degrees 2-theta.

70. The mesoporous silica film as recited in claim 68, wherein
disordered porosity is characterized by an X-ray diffraction peak between about 0.75 and
25 about 2 degrees 2-theta.

71. A method of making a mesoporous film comprising the steps of:
(a) combining a silica precursor with an aqueous solvent, a catalyst
and a surfactant into a precursor solution;
30 (b) spin coating said precursor solution into a templated film;
(c) removing said aqueous solvent, said catalyst and said surfactant
from said templated film and forming a hydroxylated film; and

(d) dehydroxylating said hydroxylated film with a gaseous silicon-based organic compound and obtaining said mesoporous film.

5 72. The method of claim 71, wherein the silicon-based organic compound is a silane.

73. The method of claim 71, wherein said dehydroxylation of said film occurs in alternating exposures of said film to a vacuum and to the gaseous silane.

10 74. The method of claim 71, wherein said silane is selected from the group consisting of trimethyl iodosilane, trimethyl chlorosilane, dimethyl dimethoxy silane, dimethyl dichloro silane, hexaphenyl disilazane, diphenyl tetramethyl silazane and hexamethyl disilazane.

15 75. The method of claim 72, wherein said dehydroxylation of said film occurs in alternating exposures of said film to a vacuum and to a silane in gaseous form.

20 76. The method of claim 72, wherein said silane is selected from the group consisting of trimethyl iodosilane, trimethyl chlorosilane, dimethyl dimethoxy silane, dimethyl dichloro silane, hexaphenyl disilazane, diphenyl tetramethyl silazane and hexamethyl disilazane.

77. A method of making a mesoporous film comprising the steps of:

25 (a) combining a silica precursor with an aqueous solvent, a catalyst and a surfactant into a precursor solution;

 (b) spin-coating said precursor solution into a templated film;

(c) removing said aqueous solvent, said catalyst and said surfactant forming a hydroxylated film; and

(d) dehydroxylating said hydroxylated film obtaining said mesoporous film, wherein said dehydroxylating includes exposing said hydroxylated film to a vapor-phase silane.

5

78. The method of claim 77, wherein said dehydroxylating further includes exposing said hydroxylated film to a hydrogen-containing gas.

79. The method of claim 78, wherein said vapor-phase silane exposing and said
10 hydrogen-containing gas exposure are alternated and repeated at least once.

80. The method of claim 78, wherein said hydrogen-containing gas includes an inert gas.

15 81. The method of claim 80, wherein said inert gas is selected from a group including argon and nitrogen.

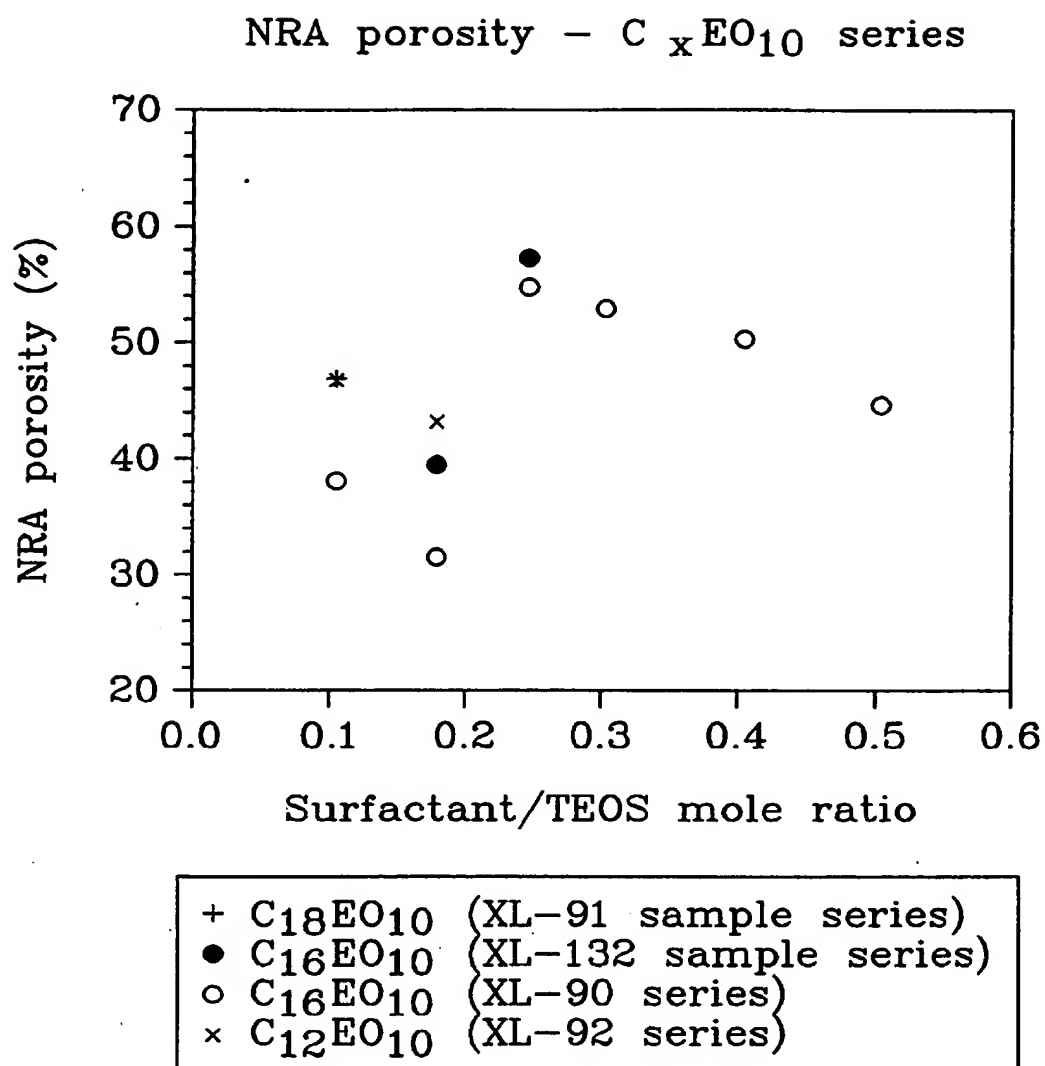
82. The method of claim 77, wherein said dehydroxylating further includes exposing said hydroxylated film to an inert gas that is substantially hydrogen-free.

20

83. The method of claim 56, wherein said acid is nitric acid.

84. The method of claim 56, wherein said silica precursor is tetraethyl orthosilicate (TEOS), wherein said aqueous solvent comprises ethanol and water, and wherein the mole ratio of water to TEOS is less than or equal to approximately 20:1.

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*Fig. 1*

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$C_{12}EO_{10}$ based Films
Surfactant/TEOS mole ratio = 0.17

Effect of Dehydroxylation Treatments on k^1

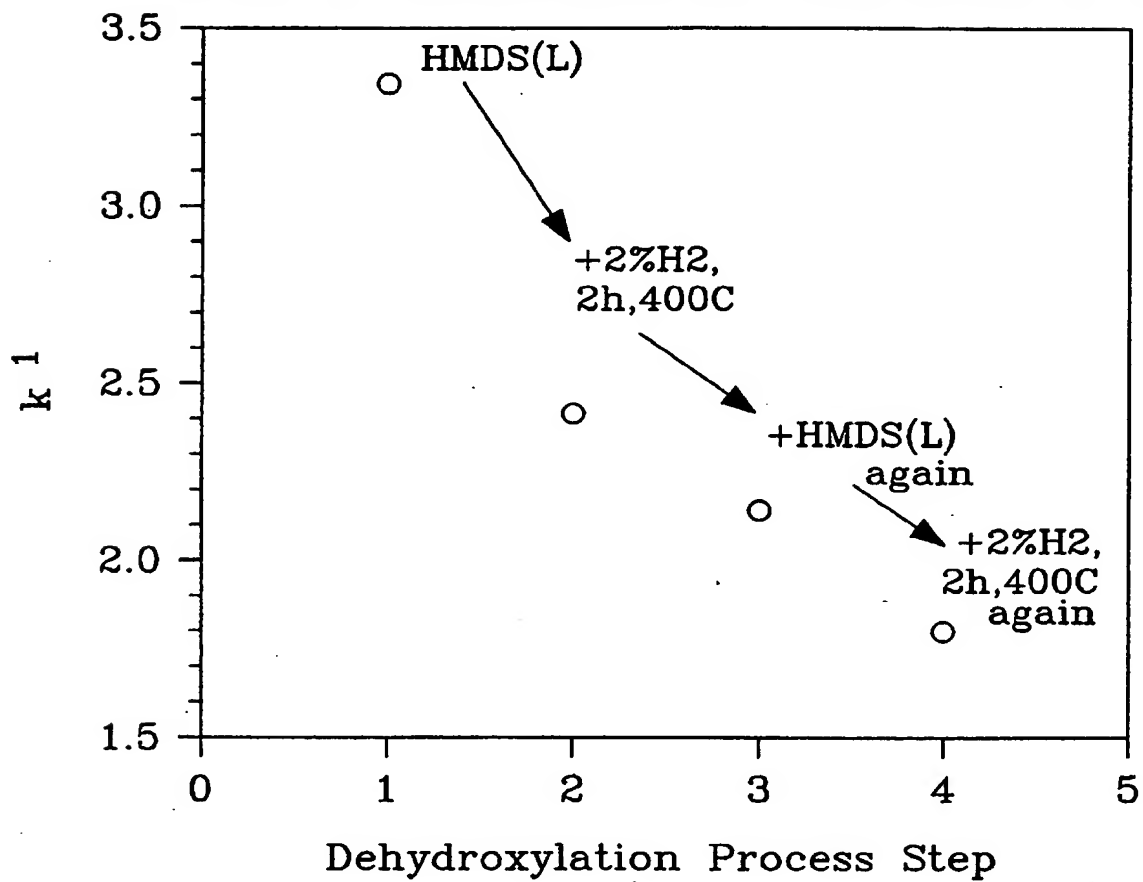
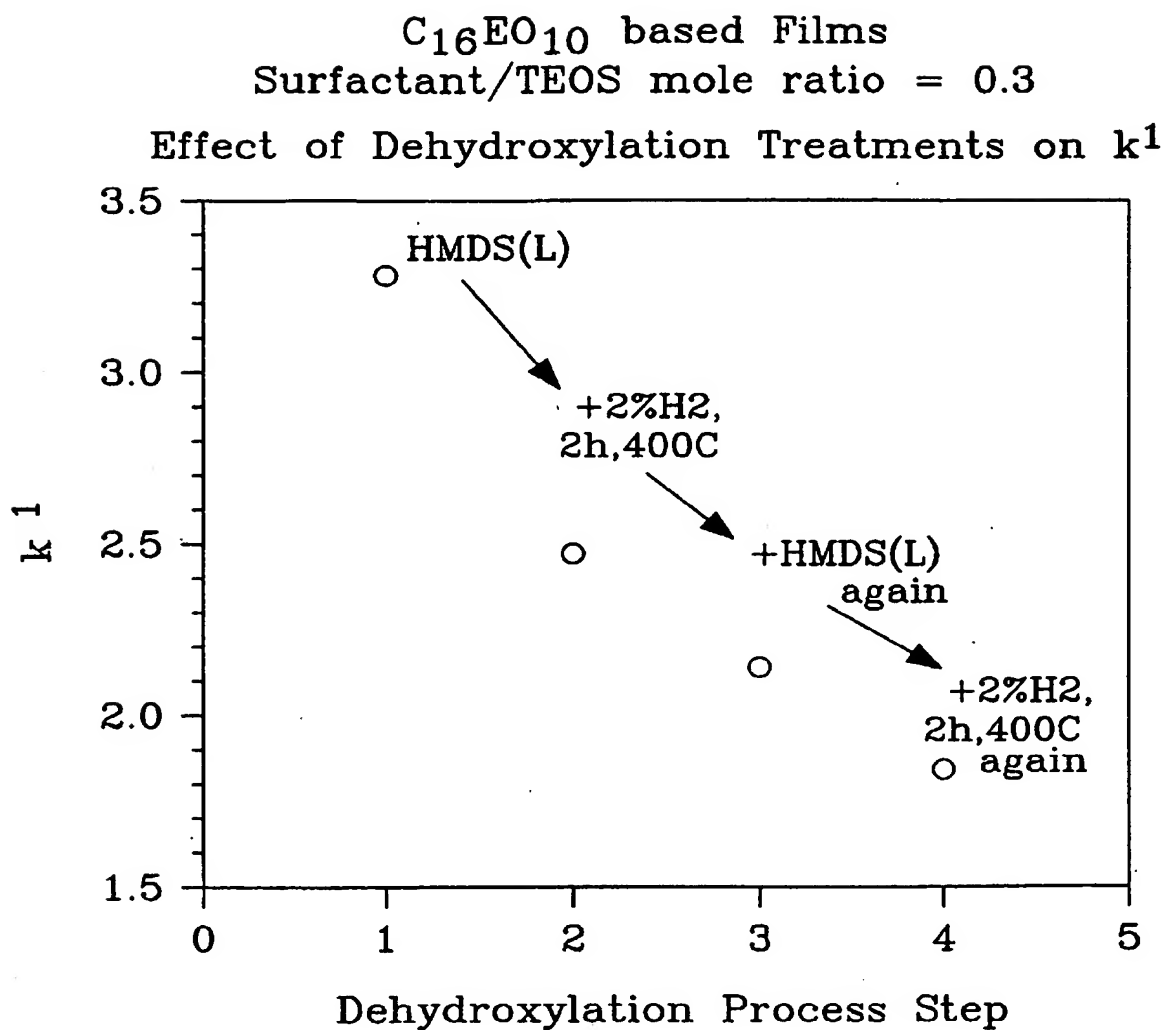
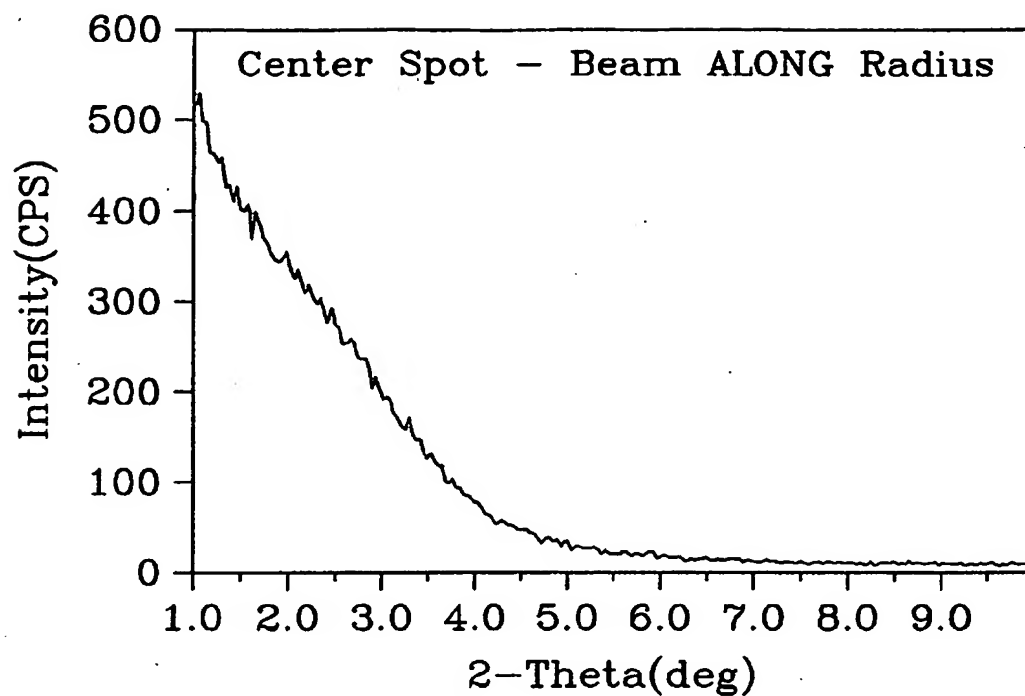
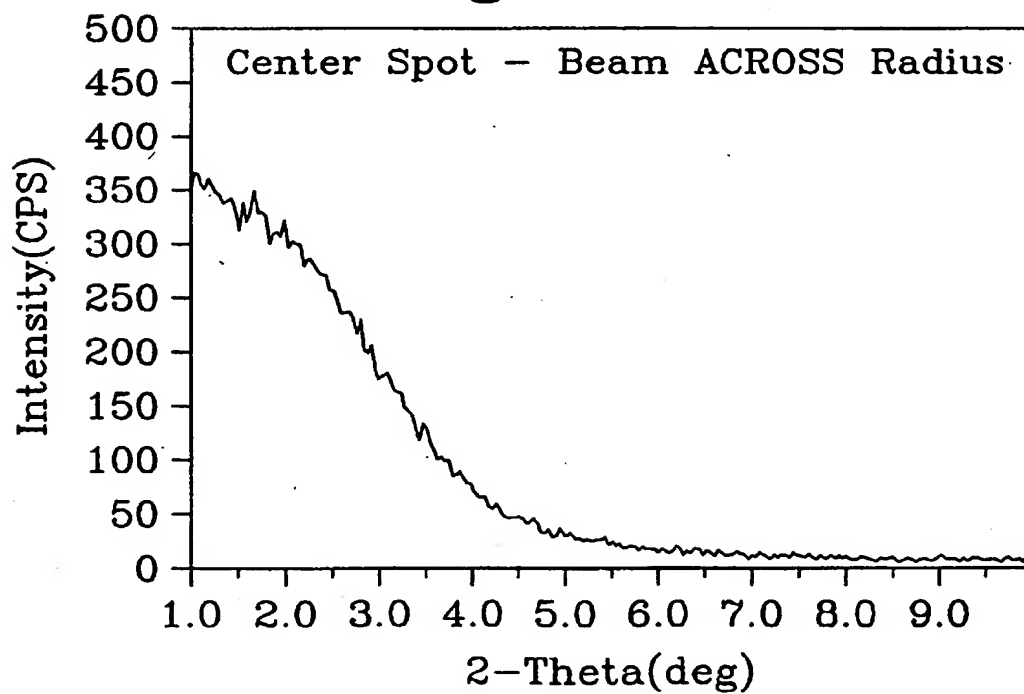


Fig. 2

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*Fig. 3*

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*Fig. 4a**Fig. 4b*

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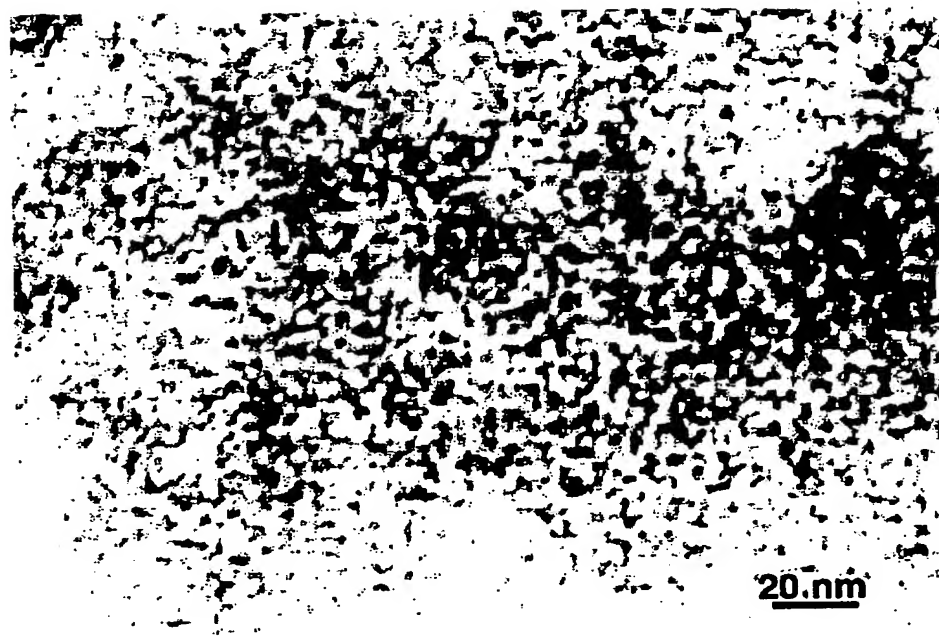
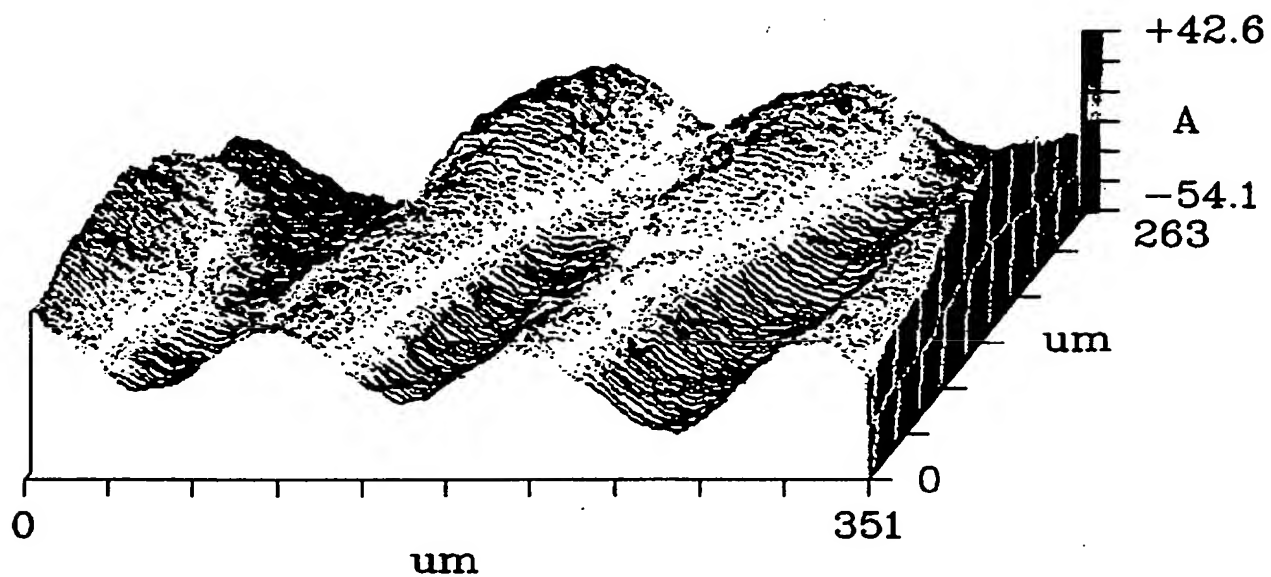
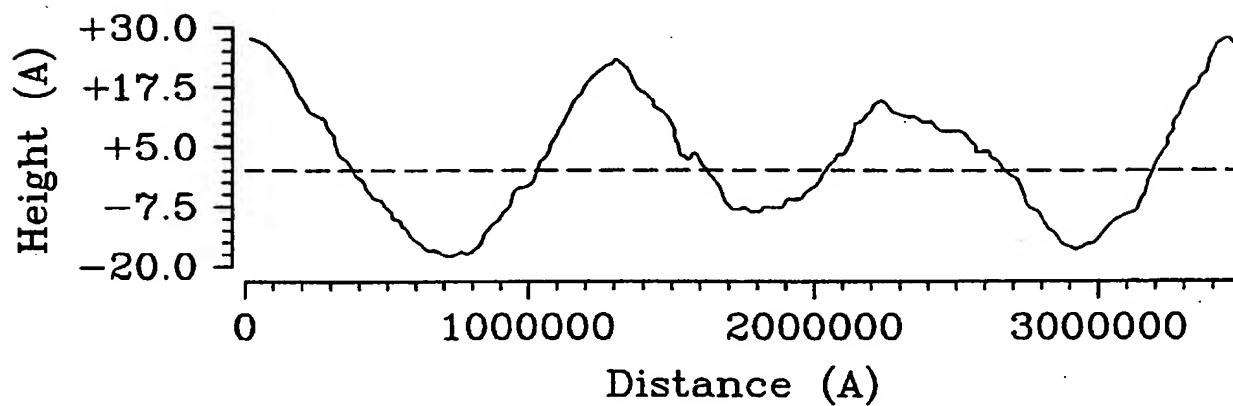


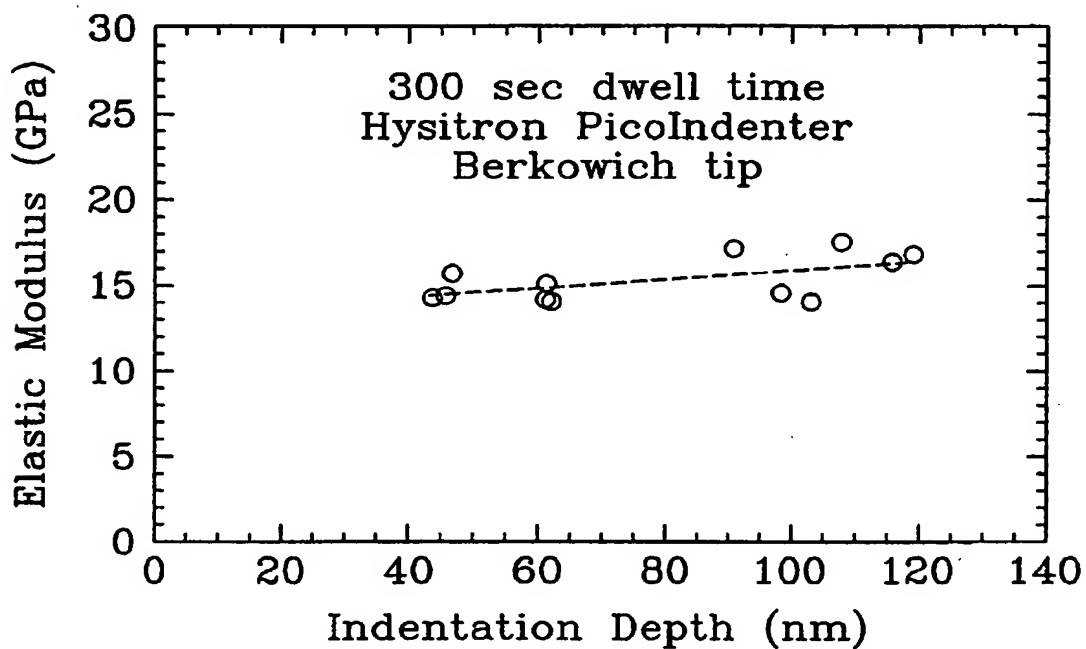
Fig. 5

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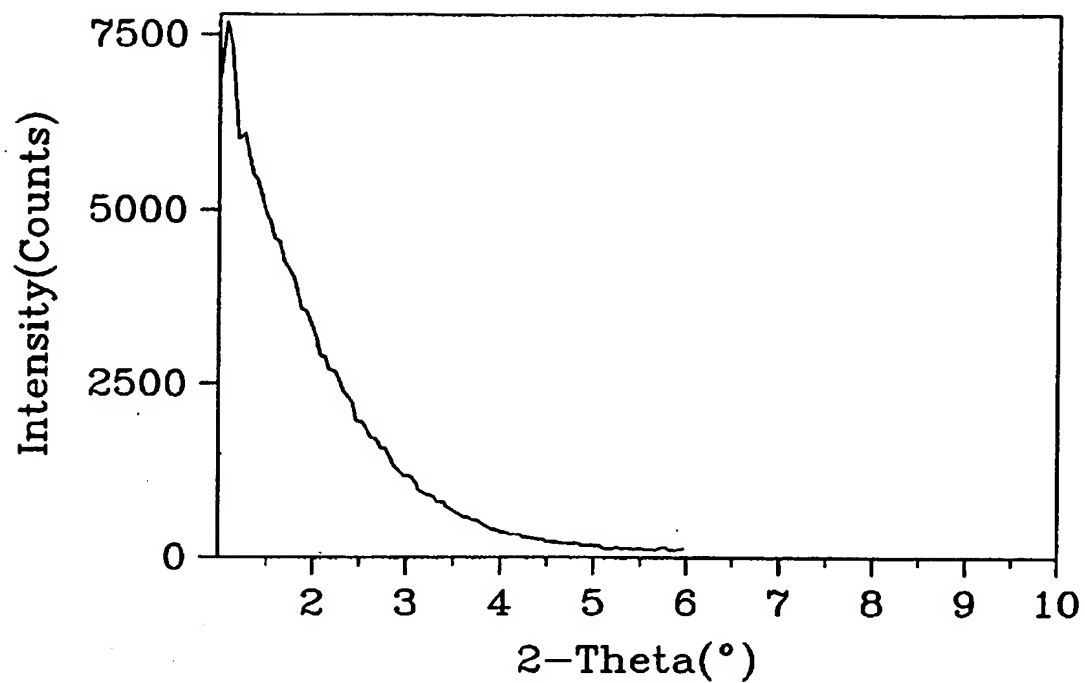
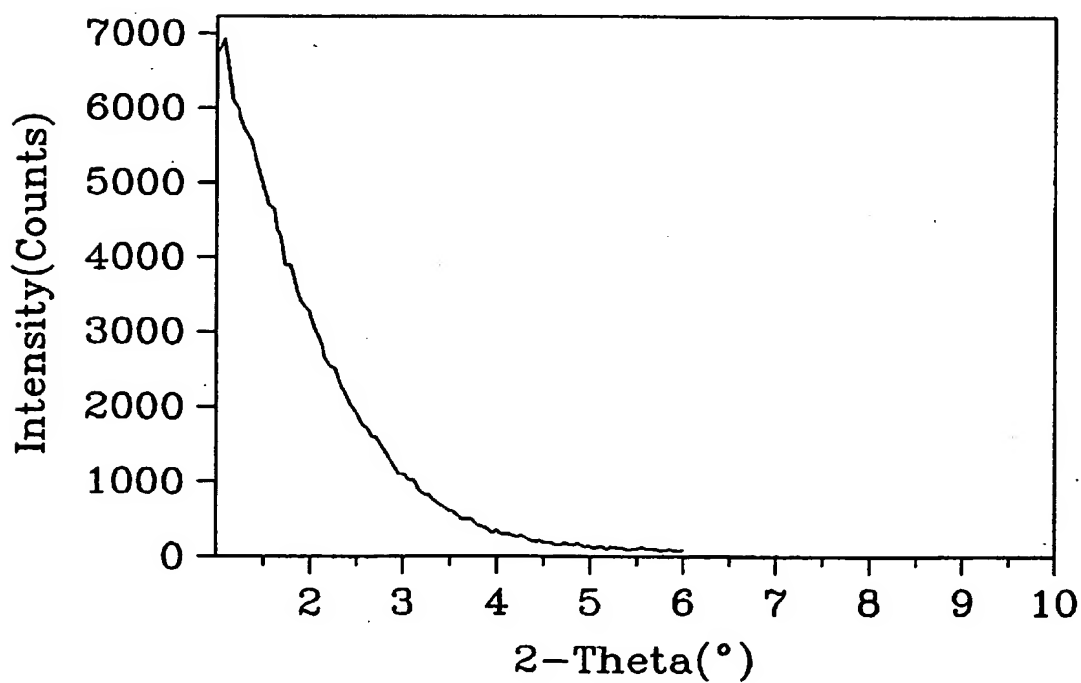
*Fig. 6a**Fig. 6b*

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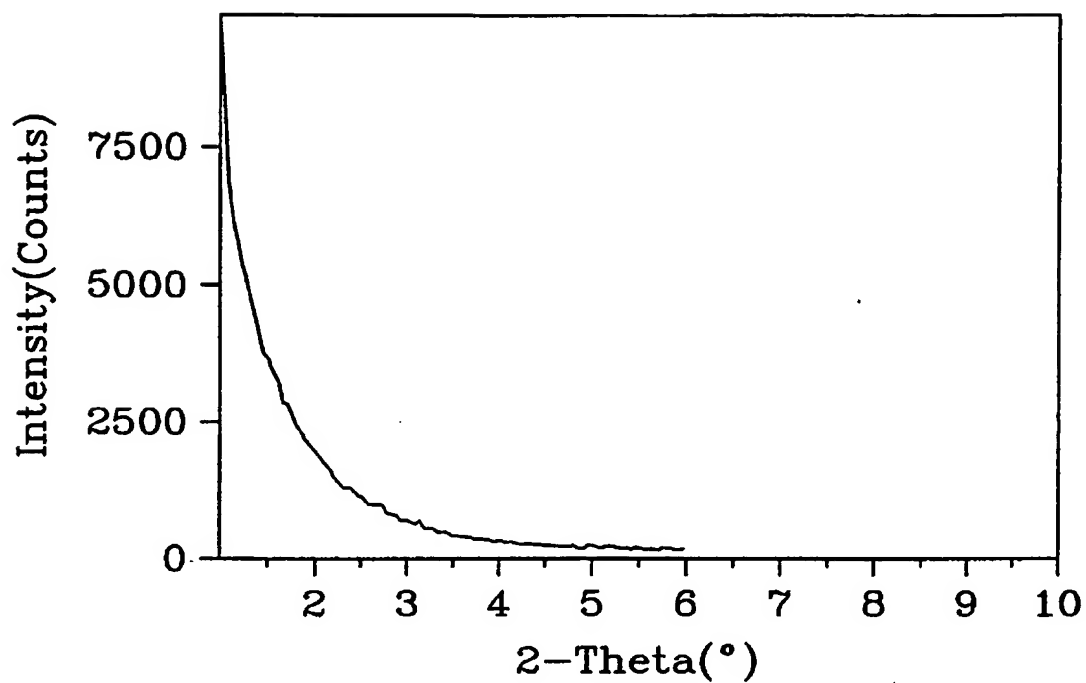
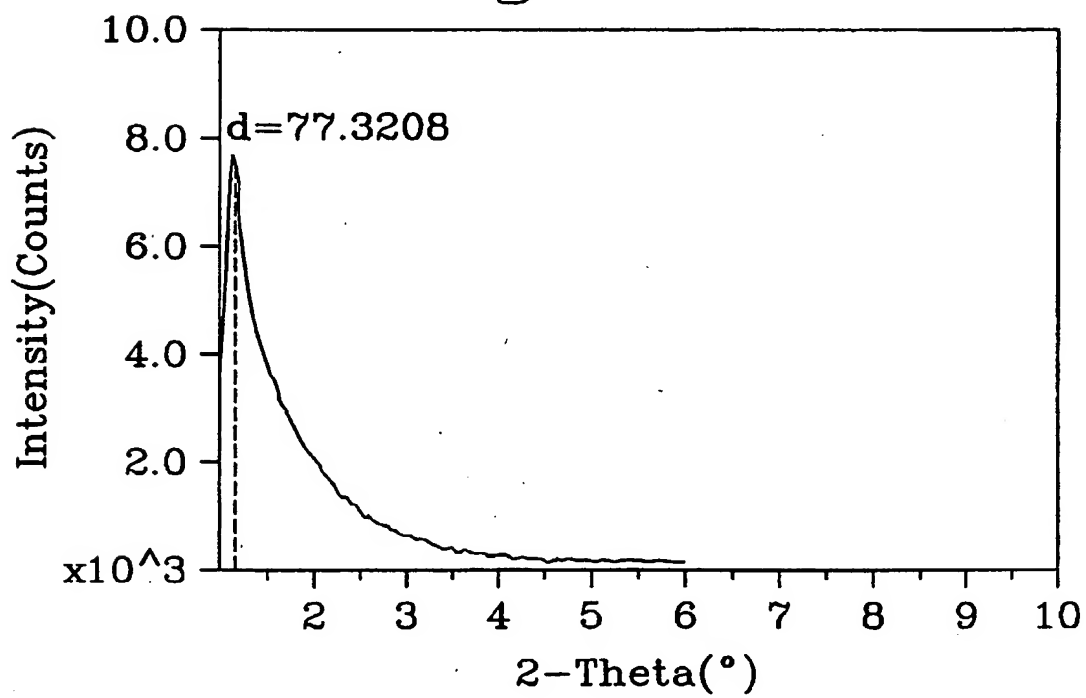
Modulus between 14 and 17 GPa
obtained for 50–300 microNewton loads

*Fig. 7*

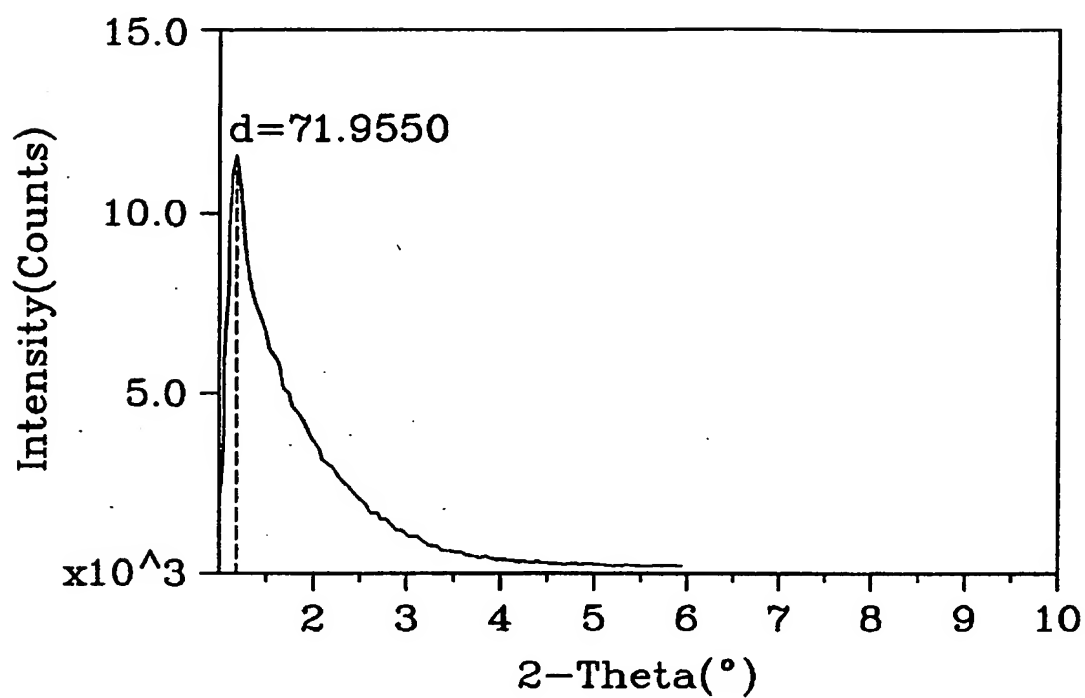
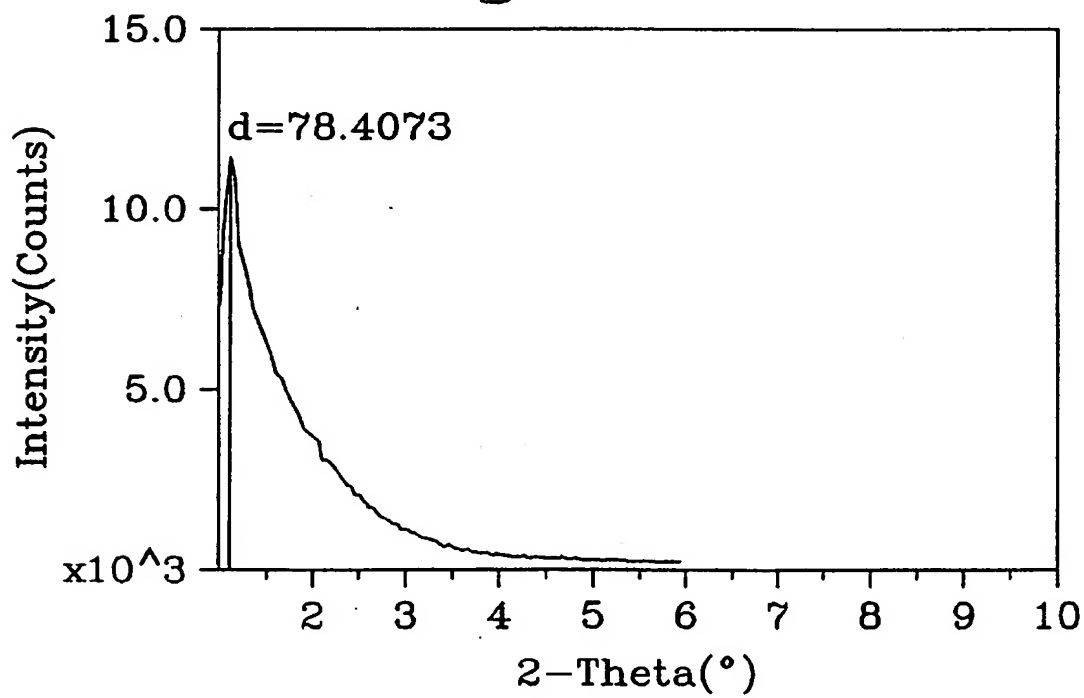
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*Fig. 8a**Fig. 8b*

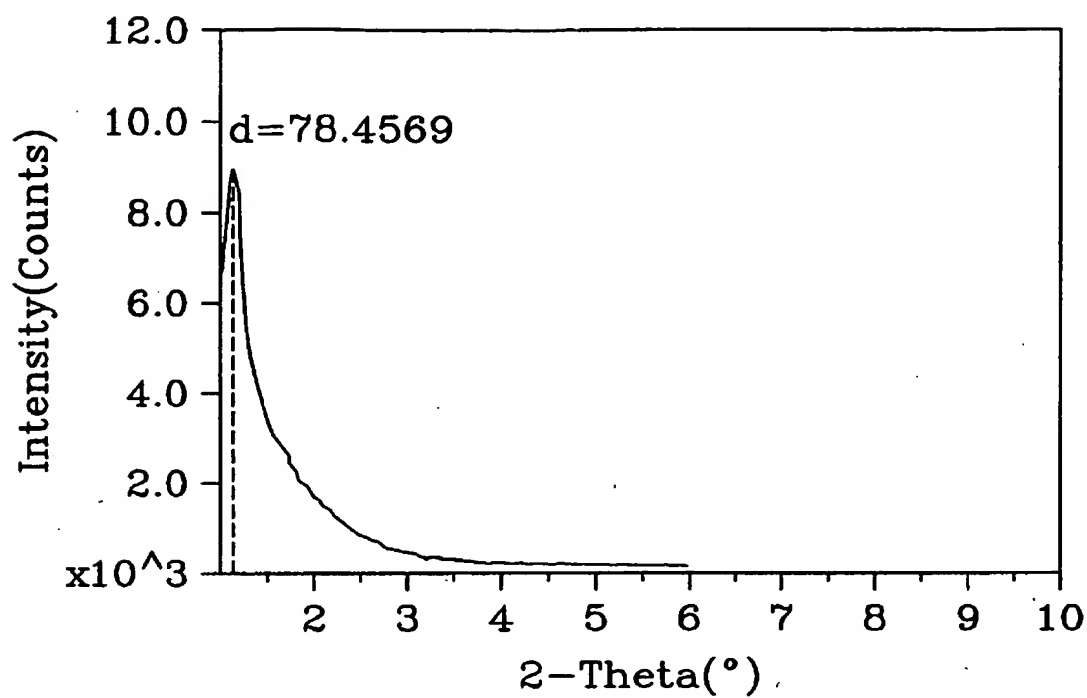
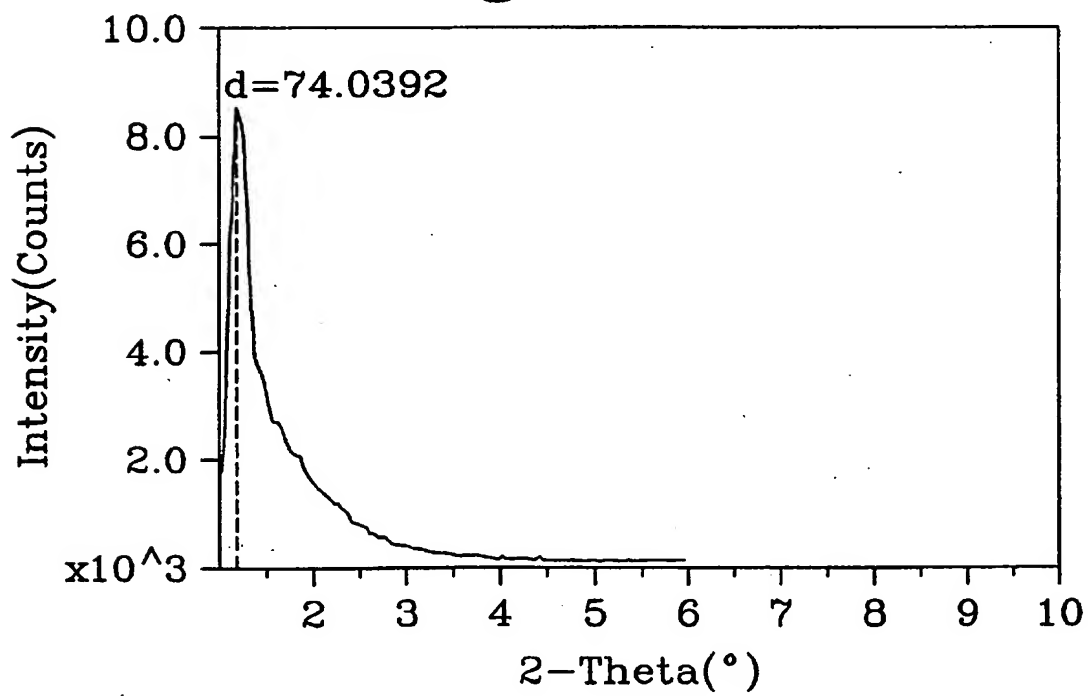
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*Fig. 9a**Fig. 9b*

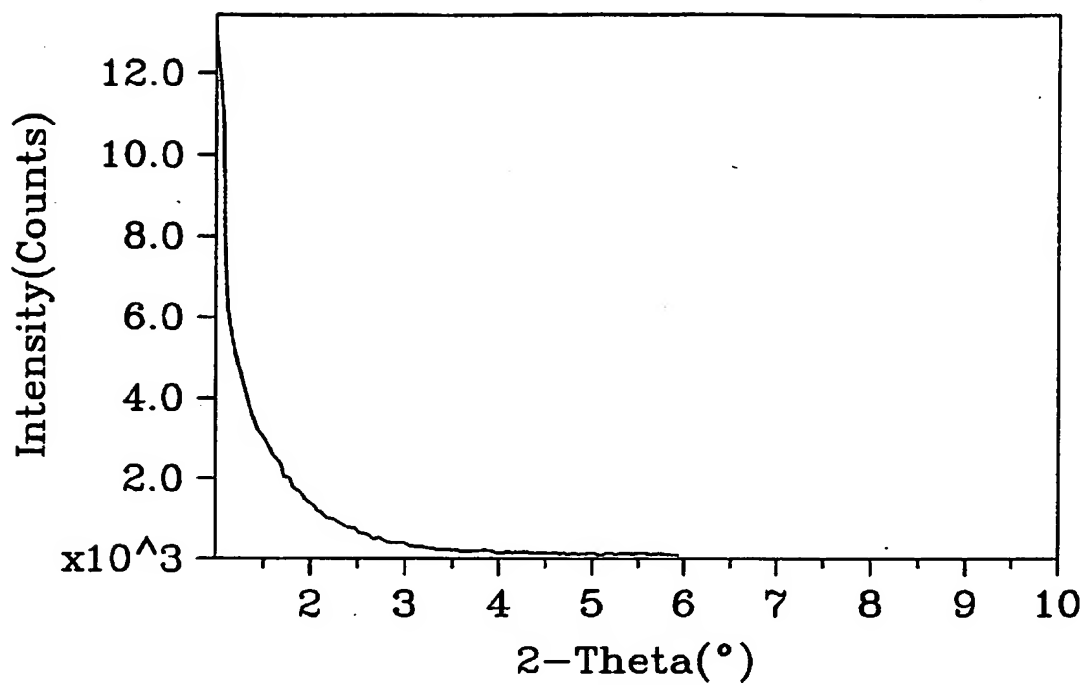
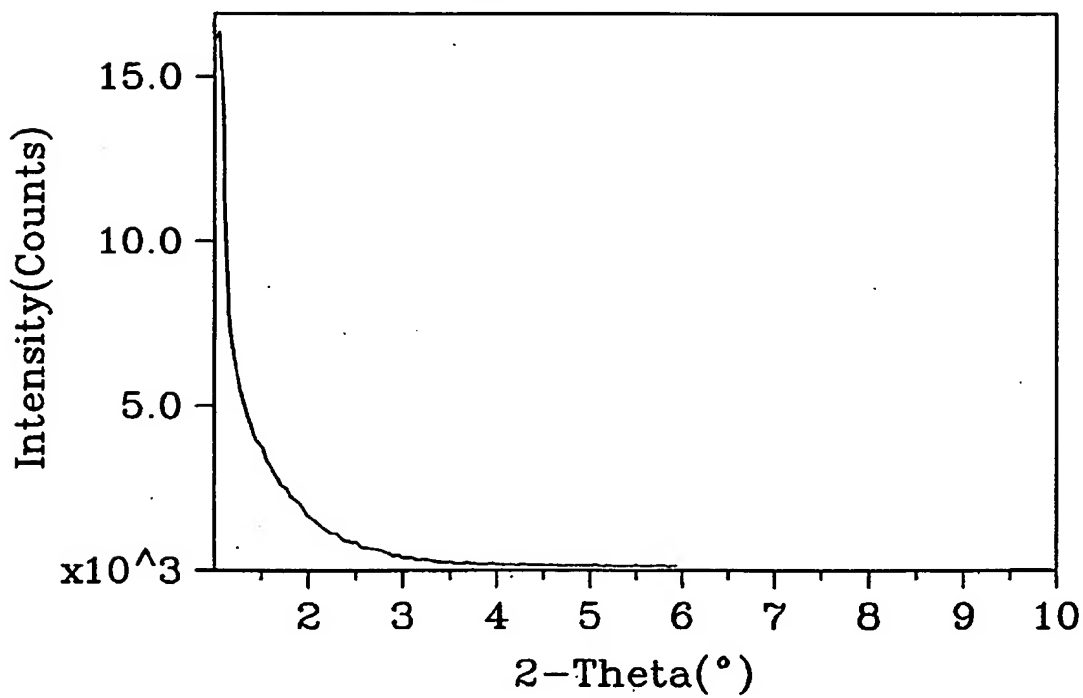
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*Fig. 10a**Fig. 10b*

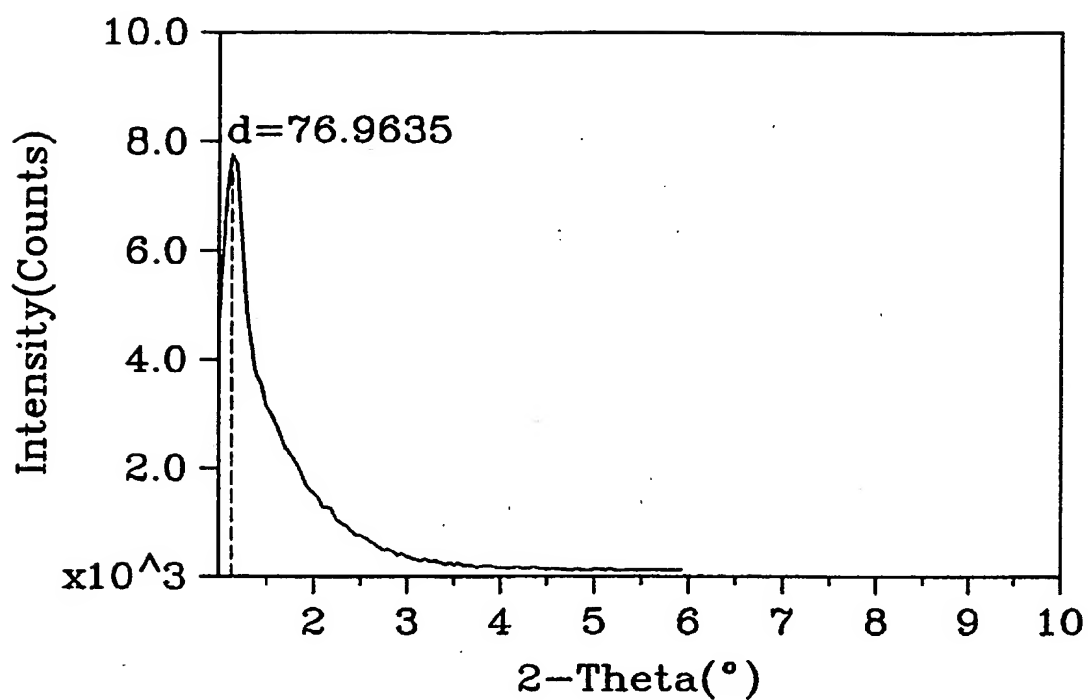
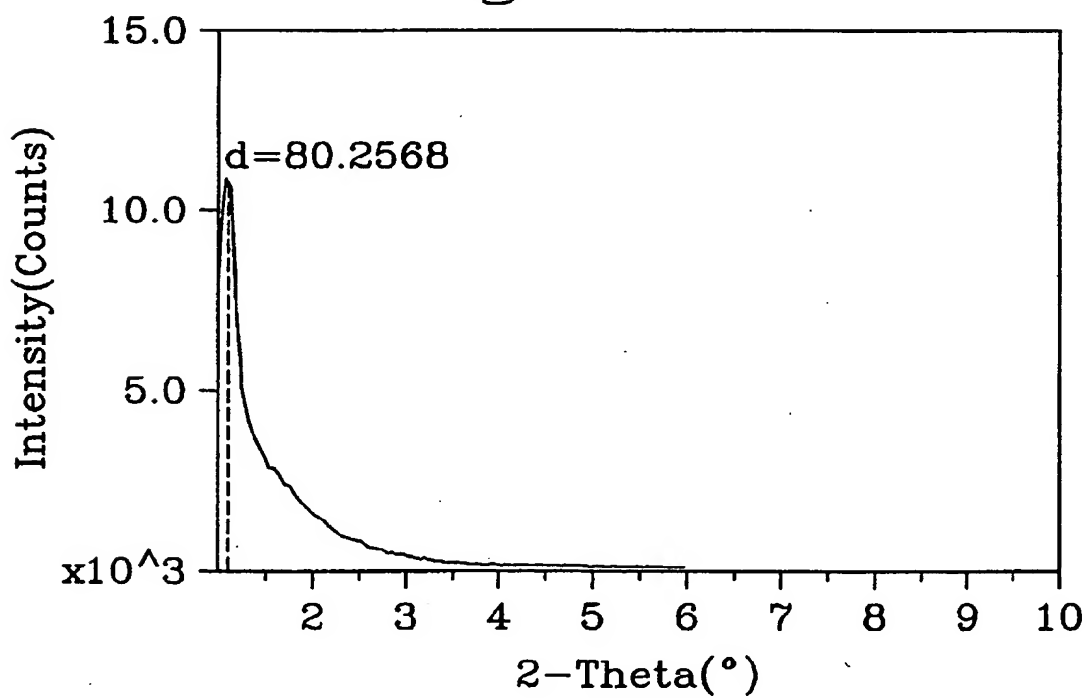
11/14

*Fig. 11a**Fig. 11b*

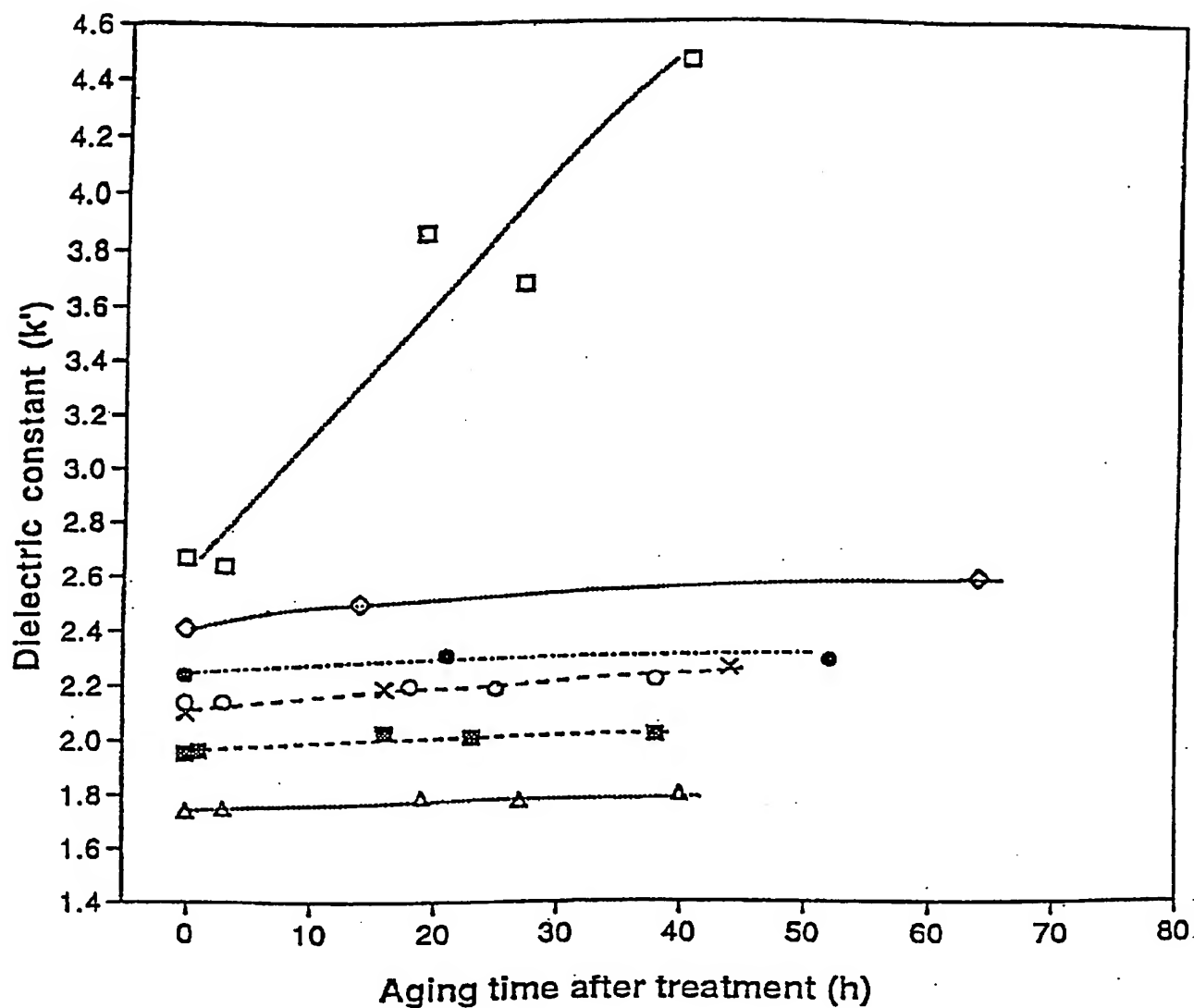
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*Fig. 12a**Fig. 12b*

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*Fig. 12c**Fig. 12d*

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□ 2%H2,2h,400°C(103-2-1-B1)

◇ HMDS (L)>>2%H2, 2h, 400°C (XL-92-2)

○ HMDS (L)>>2%H2, 2h, 400°C>> HMDS(L) (103-2-1-A1)

△ HMDS (L)>>2%H2, 2h, 400°C>>HMDS(L)>>2%H2,2h, 400°C (103-2-1-A2)

■ HMDS (L)>> Ar,2h,400°C (103-2-1-B2)

● HMDS(L)>>Ar,2h,400°C>>HMDS(L)>>Ar,2h,400 (112-1-III-D2)

x HMDS spincoat>>2%H2,2h,400°C>>HMDS spin coat>>2%H2,2h,400°C (103-2-1-C1)

FIG. 13

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/30655

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01B37/02 H01L21/316

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHAO D ET AL: "CONTINUOUS MESOPOROUS SILICA FILMS WITH HIGHLY ORDERED LARGE PORE STRUCTURES" ADVANCED MATERIALS, DE, VCH VERLAGSGESELLSCHAFT, WEINHEIM, vol. 10, no. 16, 10 November 1998 (1998-11-10), pages 1380-1385, XP000785447 ISSN: 0935-9648 cited in the application the whole document	66
A		1-3, 5, 10, 53-55

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

19 April 2000

Date of mailing of the international search report

11.05.00

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
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Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rigondaud, B

INTERNATIONAL SEARCH REPORT

Interr. Natl Application No
PCT/US 99/30655

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BRUINSMA P J ET AL: "Low k mesoporous silica films through template-based processing" LOW-DIELECTRIC CONSTANT MATERIALS II. SYMPOSIUM, LOW-DIELECTRIC CONSTANT MATERIALS II. SYMPOSIUM, BOSTON, MA, USA, 2-3 DEC. 1996, pages 105-110, XP000901682 1997, Pittsburgh, PA, USA, Mater. Res. Soc, USA ISBN: 1-55899-347-9 the whole document	66
Y		12-14, 20, 29-35, 56,57, 63,71, 74,77
A		1-3,5, 10,53-55
Y	US 5 736 425 A (SMITH DOUGLAS M ET AL) 7 April 1998 (1998-04-07) page 14, line 18 -page 15, line 24	12-14, 20, 29-35, 56,57, 63,71, 74,77
Y	XIAOMING ZHANG ET AL.: "Synthesis of transition-metal containing MSU mesoporous silica molecular sieves" CHEMISTRY LETTERS., no. 8, August 1998 (1998-08), pages 755-756, XP002135527 CHEMICAL SOCIETY OF JAPAN. TOKYO., JP ISSN: 0366-7022 the whole document	12-14, 20, 29-35, 56,57, 63,71, 74,77
A	WO 98 24724 A (BATTELLE MEMORIAL INSTITUTE) 11 June 1998 (1998-06-11) claims 1,6-10,28 examples 1,2,5 page 5, line 33 -page 8, line 12 & US 5 922 299 A cited in the application	12, 20-22, 71,77
A	EP 0 689 235 A (TEXAS INSTRUMENTS INC) 27 December 1995 (1995-12-27) page 2, line 50 -page 3, line 42 & US 5 504 042 A cited in the application -/-	12,32, 56,71,77

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/30655

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 684 642 A (TEXAS INSTRUMENTS INC) 29 November 1995 (1995-11-29) claims 1-6 page 2, line 55 -page 3, line 42	12, 29-32, 50-52, 56,71-78
A	BAGSHAW S A ET AL: "TEMPLATING OF MESOPOROUS MOLECULAR SIEVES BY NONIONIC POLYETHYLENE OXIDE SURFACTANTS" SCIENCE, US, AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE,, vol. 269, 1 September 1995 (1995-09-01), pages 1242-1244, XP000644458 ISSN: 0036-8075 the whole document	12-14, 20, 33-35, 56,57, 63,71,77
P,A	WO 99 15280 A (SANDIA CORP) 1 April 1999 (1999-04-01)	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 99/30655

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 67
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US 99 80655

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 67

The claim 67 has not been searched because this claim is not supported by the description.

The search of the claim 5,10 has been restricted to mesoporous silica film having low dielectric constant values ($k < 3$) which are stable also at ambient humid conditions.

The search of the claim 66 has been restricted to a mesoporous silica film having the claimed features.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Interr. Application No

PCT/US 99/30655

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5736425 A	07-04-1998	EP 0775669 A	28-05-1997
		JP 10087316 A	07-04-1998
		JP 10070121 A	10-03-1998
		US 5955140 A	21-09-1999
WO 9824724 A	11-06-1998	US 5922299 A	13-07-1999
		AU 5461598 A	29-06-1998
EP 0689235 A	27-12-1995	US 5504042 A	02-04-1996
		JP 8046047 A	16-02-1996
		US 5723368 A	03-03-1998
		US 5523615 A	04-06-1996
		US 5847443 A	08-12-1998
EP 0684642 A	29-11-1995	US 5470802 A	28-11-1995
		JP 8162450 A	21-06-1996
		US 5789819 A	04-08-1998
		US 5804508 A	08-09-1998
WO 9915280 A	01-04-1999	US 5858457 A	12-01-1999
		AU 9670398 A	12-04-1999